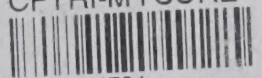


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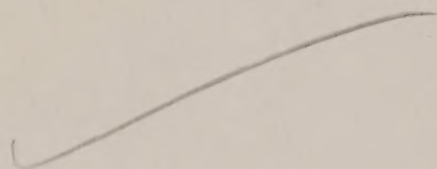
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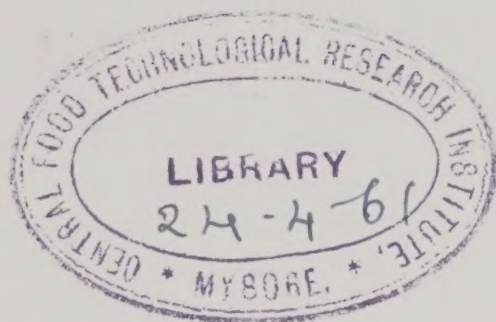
N. A. DE BRUYNE

AERO RESEARCH LIMITED, DUXFORD, ENGLAND

and

R. HOUWINK

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Adhesion and adh..

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PREFACE

This book is a symposium by specialists and it collects in one volume information about the scientific and technological aspects of adhesion.

It arose out of a discussion between us some years ago on the desirability of a book which would endeavour to deal with the subject in terms of basic scientific concepts. While we appreciated that existing knowledge was too incomplete for such an attempt to be wholly successful, we thought that it might nevertheless still be a significant contribution to knowledge. Such a book must necessarily be the work of a number of contributors and to secure some degree of continuity we arranged for the more theoretical part (Part One) to be written first and then circulated it to the authors of the technological section (Part Two). While we cannot claim that it always turned out possible to achieve harmony between the two parts of the book, nevertheless we feel that the effort has not been entirely in vain.

When one remembers that despite our growing knowledge of molecular forces it is still not possible to predict with certainty whether, say, any two given liquids will be miscible, or how strong a material will be, the difficulty of formulating a comprehensive theory of adhesion becomes apparent. Yet we think this book shows that the solution of the practical problem of adhesion need not be on entirely empirical lines.

The editors decided to leave the manuscripts from English and American authors in their original spelling, notwithstanding the fact that this may give a certain impression of non-uniformity.

We would like in conclusion to thank first of all the authors for their valuable contributions to this book. Moreover, sincere thanks are due to Miss M. HOLLANDER (Selborne) for her careful translation of many manuscripts.

Duxford, Cambridge
Delft
Spring 1951

The Editors
N. A. DE BRUYNE
R. HOUWINK

CONTENTS

PREFACE	Page V
---------------	-----------

PART ONE. THEORETICAL ASPECTS

1. GENERAL CONDITIONS FOR WETTING AND FOR ADHESION

by R. HOUWINK, *Delft*

§ 1. Conditions for a multi-layer system	3
§ 2. Conditions for wetting	3
§ 3. Conditions for adhesion	5
§ 4. Influence of the thickness of the layer	7
§ 5. Topography of adsorbing layers	7
References	8

2. MOLECULAR FORCES

by A. J. STAVERMAN, *Delft*

§ 1. Introduction	9
§ 2. Phenomenological constants	9
a. Cohesion	10
b. Adhesion	12
§ 3. Molecular constants	15
§ 4. Molecular forces	18
a. LONDON forces	19
b. DEBYE forces	20
c. KEESOM forces	20
§ 5. Molecular structure and phenomenological behaviour	21
a. Size of the molecule	21
b. Polarity	22
§ 6. Some specific data	25
§ 7. Conclusions	29
References	32

3. RHEOLOGY OF ADHESIVES

by J. HOEKSTRA and C. P. FRITZIUS, *Eindhoven*

§ 1. Introduction	33
§ 2. Rheology of adhesives before and during hardening	45
a. Application of (liquid) adhesive	46
b. Conversion of a liquid adhesive into a highly viscous form	52

	Page
c. Joining the parts	55
d. Theoretical deductions respecting tackiness	63
e. Measurement of tackiness in practice	67
f. Setting of the adhesive	71
§ 3. Rheology of hardened adhesive layers	73
Explanation of the results with thin adhesive layers, 76 — Preliminary conclusions as to joint strength, 77 — A third reason for the extra strength of thin joints, 78	
a. Plastic flow of an adhesive	79
b. Elastic modulus, as compared with that of the adherends	80
c. Expansion and movements of adhesive layers through adsorption of fluids	82
d. Internal stresses built up in the adhesive	84
e. Influence of temperature on the properties mentioned	85
§ 4. Brittleness	86
References	88

4. STATIC PROBLEMS

by C. MYLONAS and N. A. DE BRUYNE, *Duxford*

PART 1. THEORETICAL INVESTIGATIONS OF THE STRESSES IN JOINTS	91
§ 1. Introduction	91
§ 2. Torsion joints	92
§ 3. Butt joints	92
§ 4. Simple lap joints	93
a. Differential strain	94
b. Eccentricity of loading	96
§ 5. VOLKERSEN's analysis of lap joints	97
§ 6. The theory of GOLAND and REISSNER	98
a. Thin adhesive layers	99
b. Flexible adhesive layer	101
§ 7. Comparison and discussion of the results	104
§ 8. Double lap joints	107
§ 9. Gap joints	108
§ 10. Influence of the mechanical properties of adherends and adhesive	110
§ 11. Other theories	115
§ 12. Residual stresses	115
§ 13. Stresses in laminated wood	116
§ 14. Glass-to-metal seals	121
PART 2. EXPERIMENTAL INVESTIGATION OF THE STRESSES IN JOINTS	129
§ 1. Introduction	129
§ 2. The principle of similarity	130
§ 3. Extensometer tests on lap joints	132

	Page
§ 4. Previous photoelastic tests	134
§ 5. The adhesive itself as photoelastic material	136
§ 6. Models of joints made of Catalin 800.....	138
References	142

PART TWO. TECHNOLOGICAL ASPECTS

5. ORGANIC ADHESIVES

A. ANIMAL GLUES AND THEIR INDUSTRIAL APPLICATIONS

by EARL D. CORNWELL, *Chicago*

§ 1. Inherent properties of animal glues.....	147
§ 2. Preparation and handling of glue solutions	151
§ 3. Uses and general distribution of hide and bone glues	156
§ 4. Industrial applications of animal glue	157
a. Gummed paper and cloth	158
b. Surface-coated abrasives	161
c. Polishing wheels	163
d. Paper manufacture	166
(i) Paper sizings, 167 — (ii) Paper coatings, 168 — (iii) Some new applications of glue-sized papers, 169	
e. Woodworking.....	169
f. Textile processing	173
(i) Use in sizing rayon yarns, 174 — (ii) Use in rayon throwing, 175 — (iii) Use in finishes, 175 — (iv) Use as dye leveling agent, 175	
g. Calcimine	176
§ 5. Additional applications	177
a. Composition cork	177
b. Printers' rollers	178
c. Photogelatin or collotype	178
d. Bookbinding	179
e. Manufacture of toys	180
f. Use of glue in matches.....	180
g. Paint cleaner	181
§ 6. Status of animal glue industry and prospects for the future	182
Acknowledgements	182
References	183

B. VEGETABLE ADHESIVES

by WILLIAM M. LEE, *Philadelphia*

§ 1. Introduction.....	184
§ 2. Starches	185
§ 3. Dextrines	187
§ 4. Dextrine adhesives	188
§ 5. Alkali conversion	192

	Page
§ 6. Salt conversion	193
§ 7. Enzyme conversion	194
§ 8. Starch and cellulose derivatives	196
§ 9. Natural gums	197
§ 10. Acid hydrolyzed starches	198
§ 11. Starch oxidations	199
References	200
 C. SYNTHETIC RESIN ADHESIVES	
by F. CHAPMAN, <i>Duxford</i>	
§ 1. Introduction. Classification	201
§ 2. Economic significance of synthetic resin adhesives	201
§ 3. Thermosetting resin adhesives	203
a. The preparation of thermosetting resin adhesives	203
(i) Phenolic resin adhesives, 203 — (ii) Resorcinol-formaldehyde adhesives, 205 — (iii) Urea-formaldehyde adhesives, 206 — (iv) Melamine-formaldehyde adhesives, 208 — (v) Miscellaneous thermosetting adhesives, 211	
b. The solidification of thermosetting resins	214
(i) Phenol-formaldehyde resins, 215 — (ii) Resorcinol-formaldehyde resins, 219 — (iii) Urea-formaldehyde resins, 220 — (iv) Melamine-formaldehyde resins, 221	
c. Performance and applications of thermosetting resins	222
(i) Metal to metal bonding, 223 — (ii) Metal to wood bonding, 226 — (iii) Wood to wood bonding, 226	
§ 4. Thermoplastic resin adhesives	234
a. Preparation of thermoplastic resin adhesives	235
(i) Polyvinyl resins, 235 — (ii) Acrylic resins, 237 — (iii) Cellulose esters, 239	
b. The setting of thermoplastic resin adhesives	240
c. Performance and applications of thermoplastic adhesives	245
References	247
 D. ASPHALTIC BITUMEN	
by R. N. J. SAAL, <i>Amsterdam</i>	
§ 1. Introduction	250
a. Definition	250
b. Composition and structure of asphaltic bitumen	251
c. Asphaltic bitumen as an adhesive	252
d. Characterisation of bitumens	253
§ 2. Properties of asphaltic bitumen	254
a. Adhesion	254
(i) Surface tension, 254 — (ii) Contact angle, 255	
b. Rheology	256
(i) Rheology before hardening, 256 — (ii) Rheology during hardening, 258 — (iii) Rheology of the hardened layers, 258	

	Page
c. Elasticity	266
d. Breaking strength	268
e. Durability	269
(i) Influence of water, 269 — (ii) Influence of oxygen, 269	
f. Influence of fillers	270
§ 3. Properties of the system adhesive-adherends	272
a. Introductory	272
b. Processing and adhesion	273
c. Mechanical properties	274
d. Influence of time on the cemented object	275
§ 4. Concluding remarks	276
References	277

6. INORGANIC ADHESIVES AND CEMENTS

by JOHN H. WILLS, *Philadelphia*

A. INORGANIC ADHESIVES: SODIUM SILICATE	278
§ 1. Introduction	278
§ 2. Standard properties	279
§ 3. Constitution	280
§ 4. Bond strength	281
§ 5. Working properties	285
a. Viscosity	285
b. Tack	287
c. Wetting properties	290
d. Setting characteristics	293
e. Resistance to pests	296
§ 6. Anhydrous sodium silicate	296
§ 7. Reaction of sodium silicate with paper	298
§ 8. Applications of unmodified sodium silicate adhesives	299
a. Glass	299
b. Metals	300
c. Wood	302
d. Paper	304
§ 9. Corrugated paperboard	304
a. History	304
b. Specifications and tests	305
c. Manufacture of corrugated board	307
d. The silicate adhesives commonly used	309
e. Engineering characteristics of a good bond	316
f. Mechanical waste	323
g. Water and high humidity affect the bond	324
§ 10. Solid fiber board	329
§ 11. Sealing	330
§ 12. Labeling	333
§ 13. Wallboard	334
§ 14. Fiber tubes, cans and drums	335

	Page
§ 15. Insulation, etc.	336
a. Paper.	337
b. Asbestos.	337
c. Mica.	338
d. Mineral wool.	338
§ 16. Heterogeneous mixtures.	339
a. Calcium carbonate.	339
b. Starch.	340
c. Protein.	340
d. Rubber latex.	342
References.	344
 B. INORGANIC CEMENTS.	 349
§ 1. Introduction.	349
§ 2. Hydraulic cements.	349
§ 3. Plaster of Paris.	352
§ 4. Lime mortars.	354
§ 5. Sorel cement.	355
§ 6. Litharge.	358
§ 7. Iron cements.	360
§ 8. Sulfur cements.	361
§ 9. Colloidal solutions.	364
§ 10. Dental cements.	376
§ 11. Conclusion.	382
References.	383
 7. RUBBERY ADHESIVES	
by G. SALOMON and W. J. K. SCHÖNLAU, <i>Delft</i>	
§ 1. Introductory.	386
§ 2. Correlations between structure and properties of rubber adhesives.	387
a. Flexibility of raw polymers.	387
b. Vulcanization and Ebonite formation.	390
c. Isocyanates.	391
d. Tackifiers and resins.	392
§ 3. Measuring the strength of a rubber adhesive bond.	393
a. Measuring the absolute value of bond strength by the pull test.	394
b. Relative values obtained from the friction and the shear tests.	396
c. Dynamic fatigue.	397
§ 4. Fluid adhesives.	397
a. General remarks.	397
b. Adhesives based on latex.	399
c. Adhesives based on rubber solutions.	401
§ 5. The adhesion of rubber to metals.	407
a. General remarks.	407
b. Ebonite.	410

	Page
c. Thermoplastic adhesives	412
(i) Adhesives based on latex-albumen-sulphur mixes, 412 — (ii) Chlorine-containing polymers, 413 — (iii) Cyclized rubber adhesives, 415	
d. Isocyanates	416
e. Brass plating	417
§ 6. The adhesion of rubber to fibres	419
a. General remarks	419
b. Rubber-cord-adhesion	420
c. Adhesive tape	421
§ 7. Literature, references and patents	422
a. Books on rubber, rubber derivatives and rubber adhesives	422
b. References	423
c. Recent patents referring to rubbery adhesives	425

8. ADHESION IN SOLDERED JOINTS

by W. R. LEWIS, *Greenford*

§ 1. Introductory	427
§ 2. Soldering contrasted with glueing	427
§ 3. Influence of surface condition	428
§ 4. Cohesion and adhesion in soldered joints	428
a. Action of flux in soldering	429
(i) Covering action, 429 — (ii) Removal of oxide, 429 — (iii) Flux as a vehicle for reaction products, 430 — (iv) Ease of displacement by solder, 430 — (v) Electrolytic action of flux, 430 — (vi) Surface tension effects, 431 — (vii) Common Fluxes, 431	
b. Solderability of tinned surfaces	431
(i) Electrodeposited coatings of tin and solder, 432 — (ii) Chemical replacement tinning, 432 — (iii) "Stannising" and alloyed coatings, 433 — (iv) Sprayed tin coatings, 433	
§ 5. Treatment of oxidized surfaces	433
a. Aluminium	433
b. Copper alloys containing beryllium, aluminium, silicon	434
c. Glass and ceramics	434
§ 6. Wetting of metals by tin and solder	434
a. "Pores" in tin coatings	435
b. Formation of compound during spreading	435
c. Effect of surface roughness on spreading	436
d. Surface capillarity and spreading	437
e. Electrochemical action precedes spreading	437
f. Spreading and alloying	438
g. Area of spread tests for solderability	438
h. Surface tension of solders	439
j. Measurements of wetting by solder	440
k. The kollograph	440
l. Kollograph and solderability of metals	442
m. Capillary rise test for solderability	444

	Page
n. Flow dependent on temperature gradient	444
o. Fractionating effect in soldering	445
p. Penetrative powers of solders	445
§ 7. The structure of the bond in soldered joints	446
a. Compound formation	446
b. Adhesion without compound	446
§ 8. Nature of compound layers	447
a. Tin-iron compounds	447
b. Tin-copper compounds	447
c. Solubility of tin-copper compound in tin	448
d. Compound growth in joints	449
§ 9. Adhesion of anti-friction alloys to tinned surfaces	450
a. Segregation of tin-copper compound at the bond	450
b. Failure in the bond	451
c. Factors affecting bond strength	452
(i) Temperature, 452 — (ii) Thickness, 453 — (iii) Influence of flux type, 453 — (iv) Influence of cooling time, 453 — (v) Influence of tinning medium, 453	
§ 10. The effect of the rate of cooling on the adhesion	454
§ 11. Strength of solders and of soldered joints	455
a. Solders in bar form	455
b. Strength of soldered joints in tinplate	456
c. Creep strength of soldered joints	458
References	462

9. THE PHYSICAL TESTING OF ADHESION AND ADHESIVES

by N. A. DE BRUYNE, *Duxford*

§ 1. The significance of tests	463
§ 2. Tests of joint strength	465
a. Tension tests	465
b. Shear tests	467
(i) Lap joints under tensile load, 468 — (ii) The joint factor, 471 — (iii) Lap joints under compressive load, 471 — (iv) Scarfed joints, 472 — (v) Shear by bending, 474 — (vi) Tests in pure shear, 475	
c. Bending tests	476
d. Cleavage tests	476
e. Chisel tests	477
f. Peeling tests	478
g. Impact and fatigue tests	482
(i) Impact tests, 482 — (ii) Fatigue tests, 483	
h. Other destructive tests	484
(i) Knife test for plywood, 484 — (ii) Piercing test, 484	
j. Non destructive tests	484
k. Tests of tacky adhesives	485
§ 3. Durability and ageing tests	485
a. Tests at F.P.R.L., Princes Risborough, England, on wood glues	486

	Page
b. Other work on durability and ageing	486
§ 4. Some other physical tests	488
a. Viscosity	488
b. Jelly strength	489
c. Gelation time	489
d. Solids content	490
e. Flash point	490
f. Stability	490
g. Flow characteristics	490
h. Heat of reaction	491
i. Resistance to chemicals	491
References	491
AUTHOR INDEX	495
SUBJECT INDEX	504

PART ONE
THEORETICAL ASPECTS

CHAPTER 1

GENERAL CONDITIONS FOR WETTING AND FOR ADHESION

DR R. HOUWINK
Rubber-Stichting, Delft (Netherlands)

§ 1. CONDITIONS FOR A MULTI-LAYER SYSTEM

Two materials A and B can adhere by direct contact with each other; tinned iron is an example of such direct adhesion. Adhesion can also take place by intervening layers A' , B' , etc. as in the adhesion of rubber to iron through an intermediate layer of brass.

If there are n interfaces between A and B , the system can be represented by the following general picture of adhesion of n layers:

$$A / A' / A'' / \dots (n - 6) \dots / B'' / B' / B$$

The simplest case (*e.g.* tinned iron) is therefore A/B , for which $n = 1$.

From a thermodynamic point of view one has to consider two different sets of conditions, namely:

- (a) The thermodynamic conditions necessary for making the contacts at the interfaces, *i.e.*, those for *wetting*.
- (b) The thermodynamic conditions necessary of *separating* these contacts, *i.e.*, those for *adhesion*, controlling the *strength* of the joints.

For a multi-layer system the conditions must be sufficiently favourable for the complete wetting of all interfaces; the thermodynamic conditions for the *poorest wetting layer* will therefore control the final result.

For the strength of the multi-layer system the *adhesion at the weakest interface* is critical, unless the strength within the layers is less than that in the interfaces.

§ 2. CONDITIONS FOR WETTING

In order to obtain proper wetting between two substances A and B , at

least one of them has to be applied in the liquid or plastic state, sometimes in the highly elastic* state.

When a solid comes into contact with a liquid, the system will undergo changes if the free energy F can decrease, *i.e.*, if ΔF is negative. According to thermodynamics** the following equation (when volume and temperature are constant) holds true at a first approximation:

$$\Delta F = \Delta U - T\Delta S, \quad (1)$$

where F = free energy, U = internal energy, S = entropy.

There are consequently two factors controlling ΔF , namely the change in internal energy and the change in entropy. The entropy is always striving after a maximum and thus has the tendency to make $T\Delta S$ positive and therefore, $-T\Delta S$ negative. Wetting is thus in practice always promoted by the entropy factor and it depends only on the magnitude of ΔU whether wetting does or does not occur. Considering ΔU in greater detail, we realize that for wetting the solvent must be in contact with the molecules of the solid, which involves a change of potential energy.

If the molecules of the solid attract those of the solvent, heat is liberated, which means ΔU is negative. Then, according to equation (1), ΔU is acting in the same sense as the entropy factor and hence wetting occurs with certainty.

If the molecules of the solid do not attract those of the solvent as much as the solvent molecules attract each other, ΔU is positive and it depends on the magnitude of $(\Delta U - T\Delta S)$ whether wetting occurs. If in such a case ΔU is of the order of magnitude of $T\Delta S$, then slight heating will be sufficient to convert a non-wetting system into a wetting one. Experiments on dissolving have shown¹ that the case of a positive ΔU , in which, therefore, the entropy factor plays a dominant part, is more frequent than was previously expected. An example is the dissolving of rubber in hydrocarbons.

We shall now consider the energy changes in greater detail. Wetting involves² the disappearance of the surface of the solid and the appearance of the interface, leading to the following energy balance:

$$\Delta U_W = \Delta U_S + \Delta U_L - \Delta U_{SL}, \quad (2)$$

where U_W = energy of wetting

U_S = energy of solid surface

U_L = energy of liquid surface

U_{SL} = energy of interface.

Table 1 lists some of the data respecting the heat of wetting of some solids².

* For instance, when a gelatine gel sticks to a plate. The wetting by gases is not dealt with here.

** See Chapter 2 for a more detailed discussion of thermodynamics.

TABLE 1
HEAT OF WETTING OF SOME SOLIDS IN VARIOUS LIQUIDS AT 25° C
(in k.cal per molar area of liquid)

	BaSO ₄	SiO ₂	Graphite	Charcoal
Water	7.5	9.2	4.1	—
Ethyl alcohol	—	12.2	5.9	3.6
Carbon tetrachloride	9.2	—	8.3	8.1
Benzene	4.9	5.2	7.8	7.4

A practical means of measuring the wetting capacity between solids and liquids is afforded by the contact angle. It can be shown* that compatibility between an adhesive and a surface exists if approximately the same angles are obtained for the adhesive-coated surface as for the clean surface when the same calibrating medium is used to obtain the contact angles.

§ 3. CONDITIONS FOR ADHESION

The conditions for wetting in equation (2) were derived for a solid and a liquid, because this is the type of wetting that occurs in practice.

In considering the adhesion, however, one is concerned with the adhesion between the solid (S_1) and the solidified glue (S_2). This makes an essential difference, because, on breaking the joint, the interface S_1/S_2 disappears, and in its place two new surfaces appear, namely S_1 and S_2 . The energy balance is therefore:

$$\Delta U_A = \Delta U_{S_1} + \Delta U_{S_2} - \Delta U_{S_1 S_2} \quad (3)$$

where U_A = energy of adhesion.

This equation is of the same type as (2), but in (2) the factor corresponding to ΔU_{S_2} is missing.

Fig. 1 elucidates this difference which, at first sight, is unexpected.

The result of putting the solid S_1 into the liquid L (see Fig. 1a) is shown

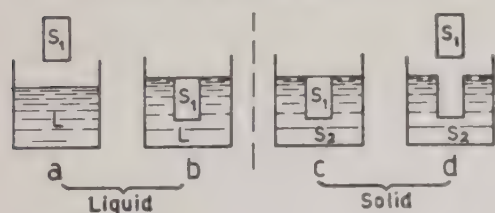


Fig. 1. Disappearance and formation of interfaces.

in b, proving that the interface has been formed and that only the surface S_1 has disappeared. This is the case of wetting. If the solid S_1 is now withdrawn from the solid S_2 (see c), the situation d results, in which the interface has disappeared and has been replaced by the sur-

face S_1 plus S_2 . This is what occurs when adhesion is destroyed.

It has been calculated² that the energy of adhesion, according to equation (3), is greater by about 1 to 2 k.cals than the energies of wetting of Table 1.

* F. MOSER, *A. S. T. M. Bull.*, Oct., 1950 p. 62. (Note added in proof).

Now the energy of adhesion will change from the instant that the glue is applied, owing to one of the following three processes:

- The solidification of the molten adhesive, due to the cooling process.
- The evaporation of the solvent.
- The chemical reaction which occurs in setting adhesives.

Re (a). If the adhesive has been solidified by cooling ΔT degrees Kelvin, $\Delta U_{S_1S_2}$ will have increased by some function of $R\Delta T$. For thermoplastics this range of cooling is, say, 75° C.

Re (b). If the adhesive has been solidified by evaporation of the solvent,

$\Delta U_{S_1S_2}$ may increase or decrease, depending on the type of solvent. How important the effect of a foreign substance on the heat of wetting may be, is demonstrated³ by Fig. 2, where small traces of water or butyric acid influence the heat of immersion of TiO_2 in benzene to a considerable extent.

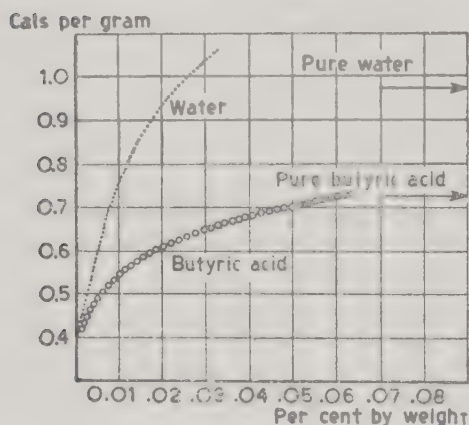


Fig. 2. Energy of immersion of TiO_2 in benzene containing some water or butyric acid

Re (c). If the glue has been solidified by a chemical reaction, $\Delta U_{S_1S_2}$ depends on the energy content of the chemical bonds formed and on the number of these bonds per mole. For a phenol formaldehyde resin with

three reactive groups, each with an energy content of, say, 70 kcal per mole, $\Delta U_{S_1S_2}$ would be of the order of 200 kcal per mole, if all bonds were formed in the hardening reaction and broken by the mechanical disruption. Actually the conditions will be far from this and so the real value will be below 200 kcal/mole.

In cases of polar-non-polar liquid molecules (stearic acid) the coherence in even layers is stronger than in odd layers, because the polar part is turned toward the solid in the first layer, away from it in the second, etc. Shearing will occur with the least opposition in the non-polar plane, marked \rightarrow in Fig. 3.

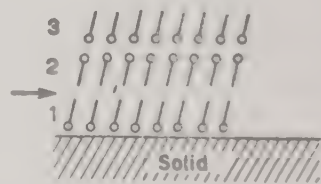
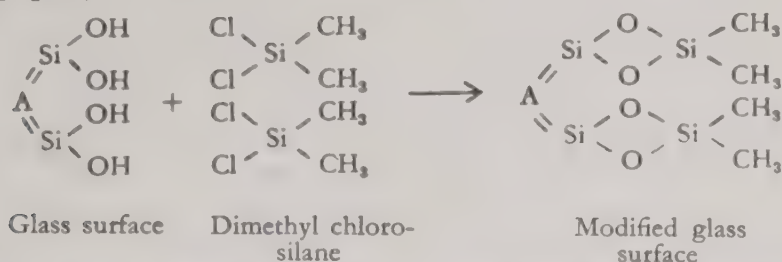


Fig. 3. Shear in a polar-non-polar liquid.

A typical example of the influence of the orientation of functional groups is the covering of glass by certain methyl silicones. A glass surface under atmospheric conditions consists essentially of exposed OH-groups. Letting

chlorosilane enter into reaction, one gets (if A represents the non-reacting part):



The new surface is now hydrophobic, repelling water molecules, thus being unable to be wetted by or giving adhesion to, polar molecules.

§ 4. INFLUENCE OF THE THICKNESS OF THE LAYER

It has been shown that the adhesion of a liquid to a solid decreases with increasing layer thickness. Table 2 shows that the energy of desorption minus the heat of vaporization for each subsequent layer is about $1/4$ of that of the layer just beneath it.

TABLE 2

ENERGY OF DESORPTION OF MOLECULAR LAYERS OF WATER FROM TiO_2 CRYSTALS³

Number of layer	Energy of desorption* (cal/mole)
1	6550
2	1380
3	450
4	80
5	30

§ 5. TOPOGRAPHY OF ADSORBING LAYERS

As the surface energy is different for the various crystal faces, edges and corners, it is clear that the adhesive strength will vary in the different crystal positions. One can therefore speak of a "topography" of the adsorbing surface. As the energy of separation of ions from the surface of a NaCl crystal varies⁴ between -1.5 and $+3.1$ units, one might say that there are "sites" of high adsorptive energy.

By measurements of the adsorption of gases on crystals, it has been shown⁵ that, in the case of VAN DER WAALS' forces⁶, ΔU is maximal when the molecules of the adsorbent can make a maximum number of contacts with the surface molecules. Consequently, the heat of adsorption is increased about four times** when, instead of being flat, the surface contains pores or chinks, in which the molecules can be adsorbed.

*The figures indicate the energy of desorption minus the vaporization energy of water in bulk.

** Under optimum conditions even 8 times.

By contrast there is adsorption by means of electrostatic forces⁶, where ΔU is maximal at sharp corners, sticking out of the surface. Due to the repulsion of dipoles with the same sign, the adsorbed molecules try to find sites, on which they are as far removed from their neighbours as possible.

There are also other purely chemical reasons for assuming the presence of sites of different adsorptive capacity. Thus there are different atomic groups on the surface. Thinking, for instance, in terms of wood and protein glues, one has the OH groups of the cellulose and the CO and the NH_2 groups of the proteins.

It is to be expected that in the initial stages of the wetting process, when the sites of high energy are the first to be saturated, the heat of saturation will be higher than at the end.

From experiments⁷ on the wetting of carbon-black by rubber it does in fact appear that initially this heat of wetting is about 18 kcal per mole, decreasing sharply until about 40 per cent. of the carbon-black surface is covered with sites of high adsorptive capacity⁸. Between 40 and 100 per cent. of this monolayer formation, the surface appears to be quite uniform as regards adsorptive capacity; as soon as the monolayer is formed, the values again decrease and approach the heat of liquefaction of the adsorbate, which is of the order of 6 kcal per mole.

Another result of the preferential forces is an orientation of the adsorbed molecules. It has been possible, for instance, to show⁵ that phenol molecules are adsorbed on NaCl by means of the OH groups, adhering to the Cl-ions, whereas the benzene ring is oriented parallel to the surface.

All these considerations lead to the conclusion that thermodynamic measurements, furnishing only overall data on heat exchanges, can only give a very rough indication of what is actually occurring.

By experiments, such as those mentioned for the investigation of carbon-black, more precise data can be obtained. These problems are discussed in greater detail in Chapter 2.

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CHAPTER 2

MOLECULAR FORCES

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§ 1. INTRODUCTION

A survey of the relationship between adhesion and cohesion on one side, and molecular forces on the other, should take cognizance of the milestones marking the passage from sheer phenomenology to a comprehensive quantitative molecular analysis.

In section 2 of this chapter we shall consider the phenomenological constants by which the phenomena can be described.

In section 3 we shall try to discover which molecular constants are decisive for the values which the phenomenological constants assume and shall deal with the relationship between both sets of constants.

In section 4 the present status of the theory of molecular forces and the general relation between molecular structure and the molecular constants of section 3 will be considered.

In section 5 we shall set forth our conclusions as to the relations between molecular structure and phenomenological behaviour.

In section 6 some quantitative data regarding molecular interaction are given and in section 7 conclusions are drawn on the question as to what we may expect from a molecular theory of adhesion and what we may not.

§ 2. PHENOMENOLOGICAL CONSTANTS

The phenomena we wish to describe are cohesion and adhesion. Of these the first is the simpler because only one homogeneous phase is involved, whereas in problems of adhesion we have to deal fundamentally with two phases of different molecular structure. However, as we shall see, cohesion of mixtures containing different molecules in a homogeneous phase closely resembles adhesion between different phases in its fundamental treatment.

(a) *Cohesion*

The most important phenomena which govern the cohesion of a material are 1) *volatility, boiling point*, 2) *solubility, miscibility*, 3) "*tensile strength*".

The quantity determining *volatility and boiling point* is the free energy of evaporation:

$$\Delta G_{vap} = \Delta H_{vap} - T \Delta S_{vap} \quad (1)$$

ΔH_{vap} is the heat needed for evaporation, ΔS_{vap} is the entropy gain on evaporation. If ΔH_{vap} has a large positive value, volatility will be low, the boiling point high; or, put differently, in equilibrium, $\Delta G_{vap} = 0$. The entropy of evaporation ΔS_{vap} depends greatly on vapour pressure p , being in fact,

$$\Delta S_{vap} = \Delta S_o - R \ln p \quad (2)$$

per mole. So for low p , ΔS_{vap} has a very large positive value and decreases rapidly with increasing p . Where the value of the heat of evaporation is high, a small p will make $\Delta G = 0$, which means that the vapour pressure will be low. An equilibrium value of $p = 1$ atm. (boiling point) can then only be reached at a high temperature T .

It will be clear that the fundamental constants which are decisive for volatility and boiling point are the quantities ΔH_{vap} and ΔS_o . One may consider these quantities per cm^3 or per gram or per mole of the substance under consideration. As, however, the entropy of a vapour at a certain p is essentially dependent on the number of molecules, it is convenient to use molal quantities when comparing different substances. Moreover, ΔS_o per mole has very nearly the same value for many ordinary liquids (*viz.* 20 cal/degree, TROUTON'S rule) and an only slightly deviating value for associating liquids. This is an additional reason for preferring to compare ΔH and ΔS values per mole.

Since ΔS_o depends little on molecular properties, the main characteristic quantity in considering vaporization is the heat of vaporization ΔH_{vap} from which a latent heat ΔU_{vap} may be split off if so desired:

$$\Delta H_{vap} = \Delta U_{vap} + p \Delta V \quad (3)$$

The quantity ΔU_{vap} per molecule being the energy needed to bring a molecule from the liquid into vacuum, might be called the cohesion energy of the liquid per molecule.

Next to vaporization, *solution* is an important phenomenon, dependent on cohesion forces. Like vaporization, the phenomenon depends on a free energy of solution, as was pointed out in Chapter 1. ΔG_{sol} consists of an energy and an entropy part.

$$\Delta G_{sol} = \Delta H_{sol} - T \Delta S_{sol} \quad (4)$$

Comparable with (2) we have

$$\Delta S_{sol} = \Delta S_{sol}^0 - R \ln c \quad (5)$$

where c is the mole fraction and ΔS is taken per mol., but (5) holds good only in dilute solutions.

Again

$$\Delta H_{sol} = \Delta U_{sol} + p \Delta V \quad (6)$$

but, as volume changes on solution are usually slight, ΔH_{sol} and ΔU_{sol} may be taken as equal at a first approximation.

The fundamental quantities decisive for the phenomenon of mixing and dissolving are ΔU_{sol} and ΔS_{sol} . Dissolving (mixing) will be satisfactory when ΔU_{sol} is small and ΔS_{sol} large. ΔU_{sol} differs from ΔU_{vap} when both are taken per molecule, in that ΔU_{sol} is the difference in cohesion energy of a molecule in the pure and in the solute state. In dilute solutions, when (5) is valid, where c is the mole fraction, it is convenient to consider ΔU_{sol} and ΔS_{sol} per mole. Generally speaking, ΔS_{sol}^0 then = 0 if both phases under consideration are liquids (phenomenon of mixing of liquids), whereas ΔS_{sol}^0 equals the entropy of fusion if one of the phases is a solid (phenomenon of solution of solids).

In higher concentrations, especially of high polymers, (5) ceases to be valid. The entropy of solution then does not depend on the molar concentration, but on the volume concentration at a first approximation and this means that the use of molar quantities is not very convenient.

The third and last phenomenon which is closely connected with the cohesion of a material we have called the "*tensile strength*". The quantity which is called technically the tensile strength is a compound quantity which contains, among other things, the negative pressure needed to separate two surfaces in the material. It is clear that this negative pressure, computed per cm², is closely related to the cohesion energy per cm³, dealt with above, and one may find the term "cohesion force" used for this pressure or "cohesion energy" for the energy needed to make two separate surfaces of 1 cm² each in the midst of the liquid. However, the cohesion energy defined in this way is definitely different from the heat of evaporation. For the energy needed to make two surfaces of 1 cm² each in a material is by definition twice the surface tension of that material, whereas the structure and the energy of the surface play no part in the heat of evaporation, since all molecules are supposed to become free.

So in tensile strength determinations we measure, besides viscosity and elasticity, a quantity which has to do with the surface tension of the material. We would do well to consider, however, that if one did actually measure the energy of separation, which is so important in tensile strength measurement,

the value found would probably be different from twice the surface tension, since the newly formed surface will not have its equilibrium structure at the moment of separation. Very little has been achieved yet in an endeavour to measure these fundamental quantities ^{1, 2}.

(b) *Adhesion*

The phenomena which we shall classify under this heading are those which fundamentally depend on the structure and therefore on the energy or free energy of a surface. Those phenomena are capillary rise or repulsion and wetting, which play an important part in the performance of adhesives.

What quantities determine whether or not a given liquid *L* will penetrate into the capillary pores of a given porous solid *S*?

These quantities are the surface tension of the pure liquid against the air (vapour), γ_{LG} and the wetting angle ϑ between the solid and the liquid. Of these, the surface tension of the liquid is the simpler, being dependent on the molecules of the liquid only. What it means and the techniques employed to measure it form the subject matter of many textbooks, so we can dispose of it briefly now. By definition the surface tension of a liquid γ_{LG} is the free energy per cm^2 of that liquid or, which comes to the same thing, the force per cm with which the surface tries to contract. It is measured by means of various methods, notably the capillary rise method, maximum bubble pressure method, drop weight method.

It might be thought that capillary rise depends on the surface tension of the liquid only and is independent of the capillary solid, since one can measure the surface tension by it, irrespective of the substance of which the capillary tube is made. This, however, is not true. The quantity which determines whether there will be capillary rise or not is the wetting angle between liquid and solid. Capillary rise occurs with a wetting angle smaller than 90° and with known wetting angle the surface tension can be calculated from the height of capillary rise. If, as in most actual measurements, the wetting angle is zero, the formulas for the relation between capillary rise and surface tension become very simple and no longer, of course, contain ϑ explicitly.

Generally in formulas

$$\gamma = \frac{1}{2} b g \rho r / \cos \vartheta \quad (7)$$

where γ is the surface tension, b the height of rise, g the acceleration of gravity, ρ the density of the liquid, r the radius of the capillary tube. With $\vartheta = 0$ this becomes

$$\gamma = \frac{1}{2} b g \rho r \quad (8)$$

It is obvious from (7) that capillary attraction (rise) occurs when $\cos \vartheta$ is positive, so for $\vartheta < 90^\circ$.

We conclude from this discussion that, in the study of adhesion, measurement of the contact angle is at least as important as measurement of the surface energy. The quantity γ , the free energy per cm^2 free surface, is a fundamental quantity directly dependent on the molecular structure of the surface and the molecular forces in the liquid under consideration. The quantity ϑ , however, is of a more phenomenological nature. The fundamental quantities behind it are the adhesive energy and interfacial energy.

Now the actual measurement of ϑ meets with some difficulties. Although there should be, of course, one single value for the energy of adhesion, *i.e.* the free energy which is gained or lost if two clean surfaces against air (vapour) are brought into contact, two, and often many more, values of the contact angle are in fact always measured. The many values found in actual measurements result from small traces of impurities on either of the surfaces. Of these "impurities", air and moisture are the most pernicious. Since the energy which is of interest here is, like any intermolecular energy, very sensitive to polar compounds, one can understand that a very polar substance like water, or an active chemical like oxygen, which forms polar oxides with many metals, may have a decisive influence on the measured quantities. If every precaution is taken to ensure cleanliness during operations, these disturbing factors can be eliminated, but the values then obtained are unrealistic and of very little practical interest.

The other difficulty, *viz.* the measurement of two definite contact angles, each of which may be completely reproducible, is more a matter of principle. These two contact angles differ, in that one is measured when the contact surface is increasing, the other when it is decreasing. There are apparently two definite and different values of the free energy per cm^2 and though one of these is, of course, the lower, both represent equilibrium. Thermodynamically, this means that both free energy values are a minimum, so to go from the one to the other state one has to pass a free energy hill. Kinetically, this free energy hill is constituted by the orientation process which takes place in the surface of both phases. Before contact, the polar parts of the molecules are as far away as possible from the surface, whereas after contact polar parts in particular may be oriented towards the surface. This suggestion would seem to be borne out by the observation that considerable differences exist between measured advancing and receding contact angles and generally very small receding angles on polar surfaces.

For the practical use of adhesives the receding contact angle, which is the smaller, seems to be the better yardstick for adhesive efficiency, since

presumably the main problem in glueing practice is not how to apply the adhesive but whether it will remain on the surface when applied. Once the adhesive has been applied, its adhesive energy is given by the receding contact angle and not by the advancing contact angle.

How, then, do we calculate interfacial and adhesive energies from a known value of the contact angle?

In Fig. 4 we have drawn the three surfaces near the contact line. The fact that equilibrium obtains means that the three forces which try to contract the three surfaces are in equilibrium

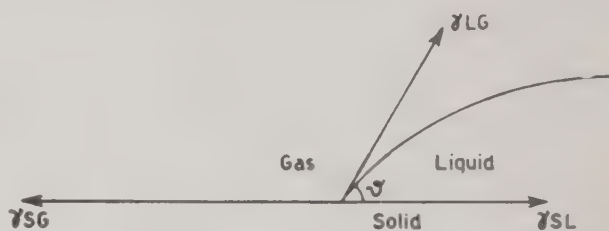


Fig. 4. Contact angle between liquid and solid.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \vartheta \quad (9)$$

where γ_{SG} is the surface energy of the solid, γ_{SL} the interfacial energy between solid and liquid and γ_{LG} the surface energy of the liquid. The surface energy of the solid γ_{SG} , which is the energy needed to make from a piece of homogeneous solid 1 cm² surface against air, does not really appear in this formula. The only quantity one finds experimentally is $\gamma_{SG} - \gamma_{SL}$, i.e., the difference in energy between 1 cm² free surface of solid + bulk liquid *L* and 1 cm² of interphase between solid and liquid. Since the solid is supposed not to change its total surface, there is no breaking up of the solid phase in the process.

With the contact angle between 2 liquids this is quite different (Fig. 5).

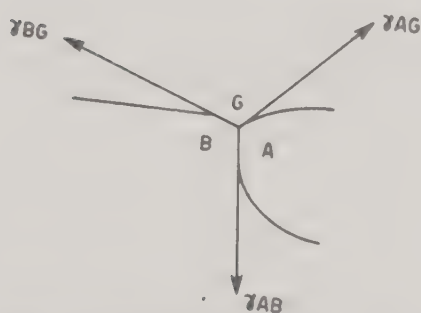


Fig. 5. Contact angle between two liquids.

Here the total surface of both liquids changes in a virtual displacement of the contact line and therefore all three γ 's play a part. However, the contact angle between two liquids is not nearly as important in practical problems as is the contact angle between a solid and a liquid.

Another way of seeing that in the measurement of a contact angle between liquid and solid only $\gamma_{SG} - \gamma_{SL}$ appears is by introducing a new quantity, the "energy of adhesion" W_{LS} , which is the energy gained if two free surfaces of 1 cm² of both solid and liquid are joined to one interphase of 1 cm². From this definition it follows that

$$W_{LS} = \gamma_{LG} + \gamma_{SG} - \gamma_{SL} \quad (10)$$

which again contains γ_{SG} only in the combination $\gamma_{SG} - \gamma_{SL}$. (10) and (9) together give:

$$W_{LS} = \gamma_{LG} (1 + \cos \vartheta) \quad (11)$$

To sum up: The quantities fundamental to problems of adhesion are:

(1) The surface energy γ_{LG} of a liquid against air, which is the energy needed to make a free surface of 1 cm², starting from bulk liquid. Sometimes $2\gamma_{LG}$ is called "the work of cohesion of the liquid".

(2) The energy difference between 1 cm² free solid plus bulk liquid and 1 cm² solid wetted by the liquid, which energy difference equals $\gamma_{SG} - \gamma_{SL}$.

(3) The energy of adhesion W_{SL} , which is the energy gained when two free cm² of liquid and solid surface are brought into contact and which is connected with the former quantities by (10).

Throughout this discussion of surface problems we have refrained from discriminating between free energy and total energy. As entropy does not play the predominant part it does in the process of solution (mixing), we shall not consider its influence in any detail. But it should be borne in mind that surface energy always means free energy and that all references to the force acting on a borderline imply its derivatives.

§ 3. MOLECULAR CONSTANTS

The constants of the foregoing paragraph are purely phenomenological. What are the molecular properties we need for an interpretation of those constants in molecular terms?

In the literature one finds a great variety of molecular properties used for this purpose, for instance "VAN DER WAALS'" constants a and b , the dipole moment, group moments, the parachor. Mention should also be made of the energy density and the dielectric constant, which, though not molecular constants themselves, do appear in formulas connecting macroscopic energy values with molecular structure.

Though certainly each of these properties has something to do with molecular energy of interaction, no quantitative theory has yet been established which describes cohesion and adhesion phenomena quantitatively with their aid.

On the other hand, very simple arguments will enable us for the most part to describe those phenomena qualitatively.

One can make an overall division between polar and non-polar substances and it is well known that polar substances attract each other, that non-polar substances attract each other but that polar substances repel non-polar substances.

This general statement of the facts, however, is not easy to expound in

terms of a more precisely formulated theory. It would, for instance, be enlightening if there were an exact number for every substance which defines its polarity and, next, some general theory explaining the difference between the "polarities" required for separation, capillary repulsion, etc. But advance along this road is beset with immense difficulties. If one tries to connect polarity with the dipole moment of the molecule, one will find that the total dipole moment is not characteristic for cohesion forces, since, *e.g.*, paradichlorobenzene, which has no dipole moment owing to its symmetry, is no less polar in its behaviour than monochlorobenzene. This difficulty is avoided by using partial moments instead of the total dipole moment, though it is difficult to know how the electrical charge distribution can be split up into partial moments in complicated molecules. What is worse is that there is no direct quantitative relation between the partial dipole moment and cohesion forces, the behaviour of molecules with a high dipole moment often being less polar than that of molecules with a low dipole moment. The only statement one can make about these relationships is that both the polar molecular forces and the dipole moment of a group have something to do with the asymmetry of the distribution of charge on that group and, therefore, if the charge distribution is symmetrical, as it presumably is in hydrocarbons and in carbon tetrachloride, both vanish. The fact is that the dipole moment is a quantity which characterizes the electric field at long distance from the molecule. Thus it does account for a contribution to the dielectric constant and also for the molecular forces in a dilute gas, as expressed in VAN DER WAALS' constant a . But in condensed systems, like liquids and solids, the molecules are so near to each other that the electric field which acts on neighbouring molecules can no longer be properly described by the dipole moment. The precise charge distribution near the point where a molecule is touched by its neighbour is dominant in cohesion forces, whereas in the integration of the dipole moment, distance of charge from the surface of the molecule is not accounted for.

Our conclusion is that the value of the dipole moment, though it has certainly something to do with polarity, is not a suitable quantity for use in a quantitative treatment of molecular forces, and the same is true for the dielectric constant.

The next thing to try for in an attempted quantitative analysis of molecular forces is the construction of a scale of polarity based upon the cohesion phenomena themselves, *e.g.*, on the data of solubility or swelling.

This procedure is exemplified in the following table borrowed from MAGAT³.

TABLE 3

LIST OF SOLVENTS, ARRANGED ACCORDING TO THEIR ENERGY DENSITY

Name	Formula	Energy density	Soluble high polymer
1. <i>n</i> butane	C_4H_{10}	6.64	<i>Numbers between brackets behind a polymer correspond to numbers of solvents for that polymer.</i>
2. butadiene	C_4H_6	6.83	
3. <i>n</i> -pentane	C_5H_{12}	7.02	
4. <i>n</i> -hexane	C_6H_{14}	7.25	
5. ethyl ether	$(C_2H_5)_2O$	7.70	
6. <i>n</i> -octane	C_8H_{18}	7.80	polythene 7.9
7. cyclohexane	C_6H_{12}	8.25	rubber (2—18) 8.0
8. carbon tetrachloride	CCl_4	8.62	buna S (4—18) 8.6
9. ethylbenzene	$C_6H_5C_2H_5$	8.75	
10. <i>p</i> -xylene	$p-C_6H_4(CH_3)_2$	8.81	polystyrene (7—19) 8.5—8.9
11. methylpropylketone	$CH_3COC_3H_7$	8.92	
12. toluene	$C_6H_5CH_3$	8.94	
13. ethylacetate	$CH_3COOC_2H_5$	9.08	
14. benzene	C_6H_6	9.21	
15. dichloroethylene	<i>cis</i> $C_2H_2Cl_2$	9.27	silicone
16. chloroform	$CHCl_3$	9.40	
17. acetone	CH_3COCH_3	9.89	polyvinyl chloride(15-21) 9.7
18. carbon disulphide	CS_2	10.0	methacrylate (9—21)
19. dioxane	C_4H_8O	10.15	
20. pyridine	C_5H_5N	10.87	dinitrocellulose 11.4% 10.72
21. <i>n</i> -butanol	C_4H_9OH	11.10	(15—28)
22. propanol	C_3H_7OH	11.92	cellulose acetate 10.9
23. nitromethane	CH_3NO_2	12.70	(15—24)
24. ethanol	C_2H_5OH	12.80	
25. cresol	C_7H_8O	13.3	nylon (25—27)
26. formic acid	$HCOOH$	13.5	
27. phenol	C_6H_5OH	14.5	
28. methanol	CH_3OH	14.8	
29. water	H_2O	23.41	

MAGAT does not place substances in order of polarity but of their energy density α . By energy density is meant the cohesion energy per cm^3 . This quantity is closely related to "polarity", as the energy density due to non-polar forces does not vary much among organic substances ⁴ and it has the advantage of being expressible by a definite number. We see from Table 3 that, if a large number of liquids are arranged according to their α , the solvents for one definite polymer do in fact come together; hence the difference in energy densities, considered as a characterising quantity, will prove a valuable guide as to whether a given polymer, p , will or will not be soluble in a given liquid, l .

MAGAT's idea, as reproduced in Table 3, was derived from a theory of mixtures, first developed for gases by VAN DER WAALS and VAN LAAR ⁵, later adapted by HILDEBRAND ⁶ to liquids. This theory can be summarized

by the well-known HILDEBRAND formula for the heat of mixing $M(N_1N_2)$ of N_1 and N_2 molecules of components 1 and 2 respectively:

$$M(N_1N_2) = \frac{N_1N_2V_1V_2}{N_1V_1N_2V_2}(\sqrt{a_1} - \sqrt{a_2}) \quad (12)$$

where V is the molar volume and a the energy density.

However, it was shown particularly by GEE⁷, who made extensive use of HILDEBRAND's theory, that the quantitative relationships predicted by this theory do not hold experimentally. So this approach, too, leads to qualitative statements only.

The reason why this treatment breaks down in an attempt to use it quantitatively is exactly the same as that discussed with reference to the quantitative evaluation of dipole moments. HILDEBRAND's theory was also evolved to account for molecular forces in dilute gases. For instance, in HILDEBRAND's treatment it is assumed that the molecular energy of interaction depends on the *distance* between two molecules as the most important parameter. Now, from our present knowledge of the structure of liquids and solids we infer that it is difficult to give even a correct definition of the distance between two molecules if both are of an arbitrary shape and are more or less entangled. We can of course arbitrarily take the distance between the centres of gravity as the important parameter, but then we know that actually molecular energy of interaction depends not only on that distance but, at a first approximation, also on the way in which superficial groups of the molecules *touch* each other, a fact already pointed out in connection with electrostatic ("dipole") forces.

Apparently the best approximation we can make of molecular forces is by assigning definite energy values to definite molecular contacts, in much the same way as proposed by LANGMUIR when he framed his "principle of independent surface action"⁸.

Starting from this principle the molecular properties of interest are:

- (a) The total molecular surface.
- (b) The energy of contact between non-polar surfaces.
- (c) The energy of contact between polar surfaces.
- (d) The energy of contact between polar and non-polar surfaces.

In reference to these quantities we shall briefly survey the theory of molecular forces.

§ 4. MOLECULAR FORCES

Molecular forces are generally divided into three classes, *viz.*,

- (a) LONDON forces, or dispersion forces.

- (b) DEBYE forces, or induction forces.
- (c) KEESOM forces, or electrostatic forces.

(a) *London Forces*

The LONDON forces are by far the most common and the most important of the three classes. They are the non-polar forces which act between all atoms, whether electrically charged or not. Of only very few, very polar molecules, like H_2O , NH_3 , do the electric forces surpass the LONDON forces. In all common organic compounds LONDON forces contribute 80–100 % of the total cohesion forces. Although they constitute the most important class, the discovery of the origin of these forces was historically the last ⁹ as it took place after the development of the quantum theory of atomic structure.

In this treatment we will not consider primary valence forces because it is very doubtful whether they are of any importance in adhesion ³⁶.

In terms of classic physics one can visualize this universal cause of attraction by considering the mutual approach of two models, each consisting of a positive core around which a negative electron is revolving. If the frequencies of the electrons are about equal, there will appear phase relations between the two atoms of such a nature that the negative electron of one atom is near the positive core of the other when the electron of that atom is at the other side, and the same thing reversed. This will result in a lowering of the total energy of the system.

It will be clear that these forces are of a very general nature. In fact, as all atoms consist of positive nuclei around which negative electrons are moving, LONDON forces exist between all atoms. Three features of LONDON forces are worth noting here.

Firstly they are fundamentally dependent on the total number of electrons present and the positive charge to which these electrons are bound. Therefore, as common groups in organic molecules like $-\text{CH}_3$, $-\text{NH}_2$ and $-\text{OH}$ or $=\text{CH}_2$, $=\text{NH}$ and $=\text{O}$ have the same number of electrons and like positive charge, they are nearly identical from the LONDON point of view.

Secondly, the LONDON forces are short-range forces, the energy declining at short distances by the 6th power of the distance and at long distances by the 7th ¹⁰.

The third important property of LONDON forces is that the energy of interaction due to these forces between unlike atoms is at most equal to the geometric mean of these energies between like forces.

$$L_{12} = \sqrt{L_{11} L_{22}} \quad (13)$$

where L_{12} is the LONDON energy of interaction between a molecule 1 and a molecule 2, while L_{11} and L_{22} are the LONDON energies of interaction between two molecules 1 and between two molecules 2 respectively.

Equation (13) has interesting consequences. As in the process of mixing components 1 and 2, a number of contacts between like molecules is broken and the same number of contacts between unlike molecules is formed, the heat of mixing is a number of times the quantity:

$$Q = -L_{11} - L_{22} + 2L_{12}$$

If (13) holds, this can be written:

$$Q = -(L_{11} - L_{22})^2 \quad (14)$$

which is always negative. So we conclude that the LONDON contribution to the heat of mixing is always negative (cooling on mixing).

(b) *Debye Forces*

The second class of cohesion forces, induction or DEBYE forces¹¹ is numerically the least important. It is the energy gained when a molecule with asymmetric distribution of charge is immersed in a polarisable medium. As these forces depend on the asymmetry of the charge distribution, they must be considered as polar forces. However, if the polarity of the molecules (asymmetry of charge) is strong, the electrostatic forces vastly surpass the induction forces. If polarity is slight, the induction forces are negligible as compared to LONDON forces.

(c) *Keesom Forces*

KEESOM¹² was the first to consider electrostatic interaction between electrically neutral molecules.

As he was in effect considering the contribution of the forces to VAN DER WAALS' a in gases, it was natural that he should develop the asymmetry of charge into dipole moment, quadrupole moment and so on, since by these quantities the electric field at long distance is approximated correctly. However, it was stated in the former section that the prevailing intermolecular distances in liquids are so short that they make this sort of development useless. In line with LANGMUIR's "principle of independent surface action", we characterize the electrostatic forces of a molecule by the activity of positive and negative spots at its surface¹³.

Energy is gained when a positive spot of one molecule touches a negative spot of another molecule.

As far as electrostatic forces are concerned, molecules can be divided into three classes, *viz.*,

- (a) Molecules with active positive spots only.
- (b) Molecules with active negative spots only.
- (c) Molecules with both positive and negative active spots.

Liquids consisting of molecules of class c are associated in the pure state. Liquids of classes a and b show no large electrostatic cohesion energy in the pure state but, when a substance of class a is mixed with one of class b , heat is released resulting from the electrostatic interaction between the oppositely charged spots. In this way we can account for positive heats of mixing and we also understand why heat absorption is so much more common than heat evolution on mixing. For heat evolution a very special electrostatic interaction between unlike molecules must obtain.

It may be noted here that the Keesom formulas containing the dipole moment are of such a nature that

$$K_{12} = \frac{1}{2} K_{11} K_{22} \quad (15)$$

K_{12} being the Keesom energy of interaction between unlike molecules, K_{11} and K_{22} between like molecules. However, by the same reasoning which leads us from (13) to (14), we see that only negative heats of mixing are obtained with this type of forces.

Let it be noted that this concept of electrostatic forces eliminates the necessity of special allowance for hydrogen bonds. The polar H-atom in alcohols, acids and amines is just a positive spot like any other, only a very active one by reason of the small size of that atom. The energy of hydrogen bonds is considered to be mainly of an electrostatic nature.

§ 5. MOLECULAR STRUCTURE AND PHENOMENOLOGICAL BEHAVIOUR

We are now in a position to equate the behaviour of substances in adhesion or cohesion phenomena with the structure of the molecules.

We shall first discuss the influence of the size of the molecule and then the influence of polarity.

(a) *Size of the Molecule*

With increasing size of the molecule ("polarity" supposed constant), the total surface increases and, therefore, the total energy needed to loosen the molecule from the condensed phase increases. As, however, the molecular volume increases at the same rate, the cohesive forces per cm^3 do not increase. So those phenomena which depend on the energy of cohesion per molecule are strongly affected by molecular size, whereas those which depend on the energy of cohesion per cm^3 are not very sensitive to size.

As the entropy of evaporation is nearly a constant if measured per molecule, the boiling point increases rapidly with increasing molecular size. Solubility and miscibility are likewise dependent on molecular size, since the entropy involved in the mixing of ordinary molecules is measured per molecule (eq. 5). Hence solubility generally decreases with increasing molecular size, except where the heat of mixing is positive or zero.

On the other hand, quantities like surface tension and energy of adhesion, being measured per cm^2 , will not depend much on molecular size. In other words, with increasing molecular size the number of contacts per molecule increases, but the number of loose contacts per cm^2 surface remains unaltered. In the case of high polymers the relations are somewhat complex. Theory shows ^{14, 15, 16} that in very dilute solutions *RAOULT's* law holds, so the entropy of solution depends on the mole fraction only.

At all usual concentrations, however, the entropy of solution depends on the volume fraction of the polymer. So in very dilute solutions the energy of solution increases linearly with increasing molecular weight and the entropy of solution is constant. But in ordinary solutions, both entropy and energy of solution, if measured per cm^3 , are constant; hence solubility will depend very slightly on molecular weight.

There is ample material to confirm these general considerations. Boiling points in particular have been analyzed very carefully and in that field one can study details like the influence of branching and other steric effects which tend to vary the effective surface of the molecule.

On close inspection of the data it is found that, with increasing total cohesion per molecule, the energy of each bond is also increased as the whole liquid becomes more dense. Particularly if a liquid is near its critical temperature is the energy of a definite contact often considerably less than in other liquids. Comparison of the molecular forces of different compounds should be based upon conforming temperatures, for instance on boiling points, but in problems of mixing and adhesion this is impossible, as the boiling points of various components may differ appreciably.

(b) *Polarity*

It follows from the foregoing section that the molecular properties which characterize polarity cannot be condensed into a one-dimensional scale, be it as scale according to dipole moments or a scale of energy densities. This accords with actual experience in selecting appropriate solvents or adhesives for specific purposes. We know that molecular interaction is too specific to be accounted for by such a scale with one variable only. In our

consideration of electrostatic forces as the interaction of definite polar surfaces, there is already greater variety of molecular properties. A molecule may either be completely non-polar (Class OO), or contain active positive polarity only (class PO), or contain active negative polarity only (class ON),

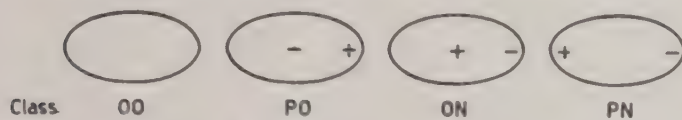


Fig. 6. Various types of molecules.

or have both positive and negative active surfaces (class PN) (Fig. 6). Even this more \ dimensional

scale of molecular properties does not account for the whole specificity of molecular interaction. In many cases a very specific fitting or non-fitting of molecules may affect the phenomena considerably.

Neglecting these special effects, let us now see how far our simple considerations take us ¹⁷.

Examples of non-polar substances (class OO) are: hydrocarbons, carbon tetrachloride, carbon disulphide.

Common substituted atoms like N, O and halogen atoms are all negatively charged. H-atoms may become positively charged if negative atoms are nearby and, as they have a very small radius, they then constitute very active positive centres. So alcohols, amines, amides and acids belong to class PN, having both positive and negative spots. Esters, ethers, ketones and pyridine derivatives belong to class ON, as their positive charge is not concentrated enough to be active. Chlorine, bromine and iodine atoms do have a negative charge, but the polar character of the halides is slight, presumably because the radius of these atoms is large. Positive spots are introduced by metal atoms in compounds like BF_3 , AlCl_3 , SiCl_3 (FRIEDEL-CRAFTS catalysts) and one also finds positive H-atoms in molecules in which several negative atoms are accumulated as in chloroform. So these molecules fall into class PO.

What are generally called polar substances are compounds from class PN, like alcohols, amines and the like. It is clear that, as molecules of these substances attract each other strongly with electrostatic forces—besides the always present LONDON forces—and as they do not find any electrostatic counterpart in non-polar compounds of class OO, they will not mix with, or adhere to, these non-polar substances. But there are no *repulsive* forces acting between molecules of classes OO and NP respectively. On the contrary, the LONDON attraction between molecules of like as well as of unlike classes is nearly equal. But the extra mutual attraction between the polar molecules is so strong that they stick together very tightly and thus **repel the non-polar molecules.**

So substances of class OO and those of class NP will mix badly and, if they mix at all, they will do so while absorbing much heat. Substances of classes PO and ON will mix very readily, with evolution of heat. They will generally mix fairly well with each of the other classes, absorbing heat in the process. The question of insolubility or immiscibility in these classes is only liable to arise where strongly polar substances, like water, are concerned. In any event, the survey given here will serve as a guide in the interpretation of evidence obtained and for the prediction of solvent or adhesive action.

It should be noted that the problems of cohesion and adhesion depend in a somewhat different way on the activities of molecular surfaces. In the process of the mixing of two liquids 1 and 2, a number of contacts 1-1 and the same number of contacts 2-2 are replaced by mixing and, as a result, the miscibility depends on

$$\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}$$

On the other hand, in the process of the capillary attraction of a liquid 1 by a solid 2, a number of contacts 1-1 are broken and twice that number of contacts 1-2 is formed. So capillary attraction depends on the quantity $\epsilon_{11} - 2\epsilon_{12}$ and not on ϵ_{22} , since no 2-2 contacts are broken nor formed. Indeed, if we try to interpret (11) $W_{LS} = \gamma_{LG}(1 + \cos \theta)$ in terms of molecular energy values we find:

W_{LS} is the energy gained on contact made between 1 cm² free surface of liquid and 1 cm² free surface of solid, so

$$W_{LS} = n\epsilon_{12} \quad (16)$$

where n is the number of contacts per cm².

γ_{SL} is the energy needed to make one cm² free surface of liquid from bulk liquid, so

$$\gamma_{LS} = \frac{1}{2} n\epsilon_{11} \quad (17)$$

(16) and (17) in (11) give

$$\cos \theta = \frac{2\epsilon_{12} - \epsilon_{11}}{\epsilon_{11}} = 2\frac{\epsilon_{12}}{\epsilon_{11}} - 1 \quad (18)$$

From (18) we see that in fact only the proportion of ϵ_{12} and ϵ_{11} is of interest for the phenomenon and that ϵ_{22} plays no part.

So if one adds a very polar liquid, 1, to a non-polar porous solid, 2, no capillary attraction will occur, as ϵ_{11} is very large and therefore $\cos \theta$ is small and θ large. But if the liquid is non-polar or slightly polar and the solid polar, then there may possibly be capillary attraction, as ϵ_{11} is small and ϵ_{12} may be of about equal magnitude.

By contrast, in the process of dissolving a substance, 1, in a substance, 2, it makes no difference whether 1 is polar and 2 not, or the reverse.

We conclude this paragraph with a few words on adhesion to metals. For our discussion in terms of polarity it is sufficient to state that metals are not polar themselves, but are extremely polarisable. If an electric charge approaches a metal surface, the metal is polarized in such a way that the electric field can be described as resulting from the approaching charge and another charge of opposite sign situated with respect to the former charge symmetrically at the other side of the metal surface (mirror image theory). So if a molecule with an active positive spot approaches the metal, a molecule with an active negative spot is induced in the metal and strong attraction results. The inference is, therefore, that polar substances in particular will adhere well to metal surfaces.

We also understand another phenomenon. Contrary to the adhesion of a polar liquid to a polar solid, in that to a metal the polarity of the metal only comes into play after the polar parts of the liquid molecules have come into contact with the metal. Now, in the pure liquid the molecules will turn their polar parts as much as possible away from the surface, as energy can thus be gained. Therefore, on coming into contact with the metal, the molecules in the surface of the liquid have to turn round, which they will have little tendency to do, because the metal has as yet no polarity. From this argument we infer that polar substances generally have receding contact angles of 0° on metals, whereas the advancing contact angle may be appreciable. Of course, the well-known surface films, always present on metals, greatly influence this effect.

§ 6. SOME SPECIFIC DATA

This Chapter has been mainly concerned with general relations between molecular forces and cohesion and adhesion phenomena without reference to specific substances. It would need at least a complete book to summarize the experimental data obtained on boiling points, heats of evaporation, of dissolving and of mixing, on solubility, miscibility and swelling capacity of specific compounds. As, however, some reference to such compounds does not seem superfluous in connection with the generalizations of the foregoing paragraphs, we have selected a few summarizing tables from the literature. We have paid special attention to high polymer systems in view of their applicability as adhesives.

First we show an often quoted table from MARK¹⁸, which gives an average contribution to molecular cohesion of various groups (Table 4). Next we show some data on heats of mixing taken from HIROBE¹⁹ (Table 5). For polyvinylchloride there are the interesting results of swelling measurements made by DOTY and ZABLE²⁰ summarized in Table 6 (p. 28). In this

table, μ is a measure of the heat of mixing, being negative when there is evolution of heat.

Though the tables confirm in a broad sense the general statements of the foregoing sections, quantitative predictions as to solubility or swelling or adhesion cannot be made yet. There are more detailed specific effects of interaction which have to be accounted for in a calculation of both the energy and the entropy of the systems before a quantitative estimate of the phenomena of adhesion and cohesion can be given.

TABLE 4
MOLAR COHESION OF DIFFERENT ORGANIC GROUPS

Group	Molar cohesion in cal per mol	Group	Molar cohesion in cal per mol
— CH ₃	1.780	— NH ₂	3.530
= CH ₂	1.780	— Cl	3.400
— CH ₃ -	990	Values which are still uncertain	
= CH-	990		
— O-	1.630	— F	2.060
— OH	7.250	— Br	4.300
= Co	4.270	— I	5.040
— CHO	4.700	— NO ₂	7.200
— COOH	8.970	— SH	4.250
— COOCH ₃	5.600	— CONH ₂	13.200
— COOC ₂ H ₅	6.230	— CONH-	16.200

TABLE 5
HEATS OF MIXING

Pair	Mole fraction of first-named comp.	Heat of mixing per mol. mixture
chloroform-ethylether	0.50	+ 647 calories
chloroform-acetone	0.50	+ 459 "
chloroform-paraldehyde	0.50	+ 533 "
chloroform-acetaldehyde	0.58	+ 289 "
chloroform-methanol	0.8	— 75 "
"	0.2	— 142 "
chloroform-ethanol	0.75	— 87 "
"	0.32	+ 149 "
chloroform- <i>n</i> -propanol	0.74	— 140 "
"	0.16	+ 99 "
chloroform- <i>isobutanol</i>	0.82	— 211 "
"	0.08	+ 21 "
chloroform- <i>isoamylalcohol</i>	0.80	— 180 "
"	0.08	+ 38 "
chloroform-ethylacetate	0.58	+ 486 "

Pair	Mole fraction of first-named comp.	Heat of mixing per mol. mixture
ethylether-acetone	0.50	— 121 calories
ethylether-paraldehyde	0.55	— 75 "
ethylether-acetaldehyde	0.46	— 135 "
ethylether-methanol	0.68	— 120 "
ethylether-ethanol	0.41	— 136 "
ethylether- <i>n</i> -propanol	0.57	— 175 "
ethylether- <i>isobutanol</i>	0.54	— 207 "
ethylether- <i>isoamylalcohol</i>	0.57	— 185 "
ethylether-ethylacetate	0.52	— 61 "
acetone-methanol	0.58	— 164 "
acetone-ethanol	0.56	— 268 "
acetone-ethylacetate	0.50	— 32 "
ethylacetate-ethanol	0.42	— 290 "
ethylacetate- <i>n</i> -propanol	0.52	— 364 "
ethylacetate- <i>isobutanol</i>	0.54	— 432 "
ethylacetate- <i>isoamylalcohol</i>	0.42	— 418 "
methanol-ethanol	0.70	— 2 "
methanol- <i>n</i> -propanol	0.67	— 23 "
methanol- <i>isobutanol</i>	0.51	— 41 "
methanol- <i>isoamylalcohol</i>	0.51	— 46 "
ethanol- <i>n</i> -propanol	0.80	— 5 "
ethanol- <i>isobutanol</i>	0.59	— 15 "
ethanol- <i>isoamylalcohol</i>	0.70	— 16 "
<i>n</i> -propanol- <i>isobutanol</i>	0.60	— 2 "
<i>n</i> -propanol- <i>isoamylalcohol</i>	0.75	— 4 "
carbonbisulfide-benzene	0.52	— 135 "
carbonbisulfide-pinene	0.65	— 90 "
carbonbisulfide-chloroform	0.54	— 127 "
carbonbisulfide-carbon tetrachloride	0.46	— 74 "
carbonbisulfide-ethylene dibromide	0.57	— 189 "
carbonbisulfide-ethylether	0.60	— 109 "
carbonbisulfide-paraldehyde	0.55	— 303 "
carbonbisulfide-ethylacetate	0.52	— 273 "
chloroform-benzene	0.56	+ 101 "
chloroform-carbon tetrachloride	0.57	— 54 "
chloroform-ethylene dibromide	0.54	+ 26 "
carbon tetrachloride-benzene	0.50	— 26 "
carbon tetrachloride-ethylene dibromide	0.48	— 122 "
benzene-penene	0.48	— 176 "
ethylacetate-benzene	0.50	— 23 "

+ means evolution of heat on mixing

— is absorption of heat on mixing.

TABLE 6
e VALUES FOR POLYVINYL CHLORIDE AND VARIOUS LIQUIDS

Liquid	e	
	53° C	76° C
trioctyl phosphate
tributyl phosphate	— 0.65	— 0.53
dihexyl phthalate	— 0.13	— 0.09
ditetrahydrofurfuryl	— 0.11	— 0.10
dibutyl phthalate	— 0.04	— 0.01
dioctyl phthalate	0.01	0.03
triethyl phosphate	0.13	0.15
diethyl sebacate	0.17	0.18
methyl amyl ketone	0.18	0.17
dihexyl adipate	0.19	0.23
diamyl sebacate	0.24	0.24
nitrobenzene	0.29	0.29
valerolactone	0.32	0.30
dimethyl sebacate	0.34	0.34
dihexyl sebacate	0.35	0.36
tricresyl phosphate	0.38	0.38
di- <i>n</i> -octyl succinate	0.39	0.39
bromonaphthalene	0.40	0.38
butyl acetate	0.40	0.41
diethyl phthalate	0.42	0.40
mesityl oxide	0.43	0.42
dibutylcellosolve phthalate	0.44	0.42
nitropropane	0.44	0.42
ethylene dichloride	0.46	0.43
ethyl acetoacetate	0.49	0.46
anisole	0.515	0.49
chlorobenzene	0.53	0.50
dimethyl phthalate	0.56	0.53
dibenzyl sebacate	0.56	0.52
tetraethyleneglycol dipelargonate	0.56	0.55
methyl acetyl ricinoleate	0.56	0.56
methylcellosolve acetyl ricinoleate	0.57	0.57
di-2-ethylhexyl sebacate	0.59	0.57
acetone (at 27° C, 0.63)	0.60
butyl acetyl ricinoleate	0.65	0.67
nonaethyleneglycol dipelargonate	0.71	0.66
benzene	0.77
polymerized butyl acetyl ricinoleate	0.78	0.78
butyl ricinoleate	1.22	1.20
octyl laurate	1.38	1.41
decyl pelargonate	1.47	1.43
dilauryl phthalate	1.75	1.41
butanol	1.74	1.58
butyl palmitate	1.73	1.66
ethyl stearate	1.73	1.52
dioctyl ether	2.6	2.8

These tables generally confirm our qualitative considerations: hydrocarbons, carbon-tetrachloride and carbon bisulfide are non-polar; alcohols, acids, and amines are strongly polar on both sides; esters, ketones and

ethers are strongly polar on the negative side, partially chlorinated hydrocarbons are polar on the positive side.

On the other hand, it typifies the situation with regards to a quantitative molecular theory of adhesion that even for such a simple quantity as the heat of mixing of liquids no quantitative theory exists.

§ 7. CONCLUSIONS

Surveying this chapter, we come to the conclusion that the path which will ultimately lead to a complete understanding of characteristics of adhesives from the properties of their molecules is very long and very thorny. Many sections of this road have not yet been cleared by science. Before any substantial progress can be expected, both our theoretical insight and our knowledge of quantitative data have to advance on many points and, in view of the difficulties involved even in the estimation of a simple quantity like cohesion from molecular data, we have no warrant to expect an early acquisition of sufficient knowledge to say, with certainty, *which* measurable quantities describe the desired relations and how they are measured. In fact, the obstacles to a theoretical understanding sufficient to enable us to predict adhesive properties from molecular quantities are such as to make efforts in this direction well-nigh hopeless from the technologist's point of view. This means that, for the time being, significant improvements in the field of adhesives must be expected from direct trials by technologists, rather than from theoretical predictions by pure scientists. On the other hand, even if large blanks will have to be filled in before comprehensive scientific knowledge can be obtained, unconnected gains of theoretical insight into some of the factors responsible for the specific properties of adhesives may afford valuable guidance for technological research. We will, therefore, briefly survey the many elements which a complete molecular theory of adhesive properties would of necessity have to contain.

First the question whether a given adhesive will adhere strongly to a given material is not only determined by the capillary constants, considered in this chapter, but also by the hardening process. One factor which seems to be of primary importance is the shrinkage on hardening, adhesion being strong when the shrinkage is small. Of course, the influence of shrinkage may be diminished by a high elasticity of the adhesive, since the extent to which a shrinking layer of an adhesive can remain in contact with a material of constant dimensions depends on the ratio between the force of adhesion (which, if calculated per cm length, equals the surface energy per cm) and the force necessary to counteract shrinkage. The latter force depends on

the product of elasticity modulus and extent of shrinkage of the adhesive. Now, we are not altogether bankrupt where theoretical knowledge of the elasticity of polymers is concerned^{21, 22}; there is, generally speaking, a perceptible tendency for low elasticity modulus to go hand in hand with a small number of cross-links and only slight polarity of the molecular groups between the knots. Where hardening is a physical process (*i.e.* evaporation or absorption of solvent), shrinkage can be calculated from the concentration of the polymer in the glue applied; but our knowledge of the factors governing shrinkage in cases of hardening due to chemical processes, such as polymerisation or polycondensation, is scanty, though there is evidence to show that ring-chain polymerisation results in only very slight shrinkage²³.

In practice the effect of shrinkage is certainly as important as that of capillary forces; therefore both theory and technology of adhesives should take shrinkage into careful account.

The circumstances being what they are, it will be clear that capillary forces like intersurface energy are not amenable to direct estimation by adhesive strength measurements, particularly as many effects besides those mentioned come into play in actual adhesion tests²⁴.

Since, then, neither the characteristic molecular quantities nor the characteristic phenomenological quantities can yet be measured directly or even calculated from a combination of measurements, attempts to correlate any molecular quantity like the dipole moment with any phenomenological quantity like adhesive strength cannot be expected to yield more than a very general and qualitative impression.

Attempts in this direction have been reported on various occasions. MC. BAIN and LEE²⁵ were the first to recognize the multitude of factors involved in adhesion and also to reveal a rough correlation between the melting point of organic substances and the adhesion to metals.

DE BRUYNE²⁶ and also DOOLITTLE and POWELL²⁷ stress the importance of polar groups.

A more recent study has been made by McLAREN and collaborators^{28, 29, 30, 31, 32}, particularly on the adhesion of polymers to cellulose.

In²⁸ they reveal a linear relation between the logarithms of carboxyl-concentration of a polymer and of the adhesion of that polymer to cellulose. This work is an improvement on older work because of their attempt to calculate well-defined physical constants from their measurements, in particular energy values from the slope of the logarithm of measured quantities versus the reciprocal of T . On the other hand, it is clear that the validity of the quantitative relations which they find is very limited.

In ³⁰ the compound phenomenological quantity "adhesion" is correlated with an other compound phenomenological quantity, "tack temperature", and with the dipole moment of the molecules. Though relations of this kind may be very helpful in guiding research, they contribute little to the solution of our general problem. In ³¹ yet more factors are considered, such as molecular weight, intrinsic viscosity and humidity and also general observations are made on the conditions for adhesive and cohesive failure respectively.

In an interesting paper THINIUS³³ makes some general statements about the gluing of polymers. He remarks that polymers of "different polarity" but soluble in the same solvent cannot always be glued together with solution of one of the components in that solvent. He attributes this to repulsion of the molecules of different polarity and finds that adhesion can be obtained by adding an intermediate layer of "intermediate" polarity. As an example he quotes the combination nitrocellulose and polyvinylchloride, which cannot be glued with the common solvent cyclohexanon, but which yields good results with an intermediate layer of a vinylacetate copolymer or the like.

THINIUS' ideas fit very well into our general picture if only by "different" polarity we understand difference of degree and not of sign. It is well known that solutions of different polymers in the same solvent are generally, though not always, incompatible, which means that they separate when added together. This is caused by the fact that the entropy of mixing is often too small to overcome a negative heat of mixing. However, macromolecules of *opposite* polarity will mix very well, if the solvent does not interfere, and one would expect good adhesion for such combinations with suitable solvent.

For the molecules of polarity of different degree, THINIUS' solution with an intermediate layer of copolymer can be understood and even more so if this copolymer contains groups of polarity *opposite* to that of the components. This, indeed, seems to hold for the acetate-copolymers of vinylchloride.

In concluding it may be remarked that in this chapter mainly the physical factors determining the strength of the ready glued joint have been considered. Though we have here ignored the kinetics of the hardening process, the importance of this aspect of adhesive quality should by no means be underestimated. Much research is, in fact, being conducted on the subject and considerable progress in the technology of adhesives may be expected from improvements in the technique of hardening, either by better catalysts or by more suitable polymerisable substances. The kinetics of polycondensation-reactions, however, is a science in itself ³⁵ and cannot be treated here.

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CHAPTER 3

RHEOLOGY OF ADHESIVES

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§ 1. INTRODUCTION

Rheology is a rather recent branch of physics, originating not so much from new developments in physical science itself, as from an urgent need for those occupied with the chemistry and technology of fluid and plastic materials to acquire systematic knowledge of the mechanical behaviour of these deformable materials. Being part of physical science, its method is to start from certain assumptions about the relationship between force, deformation and time in very small areas of the material considered, thus arriving at conclusions about the deformation of whole bodies along known

(though sometimes elaborate) mathematical paths. The newcomer, usually a chemist, is inclined to regard these mathematical complications as the crucial point of rheology. In fact, the choice of adequate basic assumptions is most important. We will try to give a simple exposition of those principles of rheology which would account for the mechanical behaviour of adhesives during their application and in their function as binding agents. In doing so, the great difficulties inherent in the choice of adequate assumptions will become evident.

Simple fluids are called Newtonian, because they follow NEWTON's law:

$$D = \frac{\tau}{\eta} \quad (1) \text{ (See Fig. 7).}$$

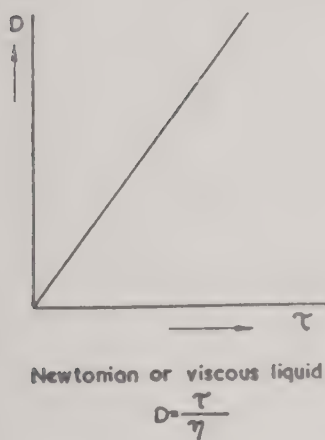


Fig. 7. Rate of shear strain D as a function of stress τ for a Newtonian liquid.

This law refers to the effect of a shearing stress, of τ dynes/cm² working on parallel planes. If one takes (see Fig. 8a) a small parallelepiped with a top surface of ΔO cm² and a thickness of dy cm, then a force of $\Delta O\tau$ will pull the top surface of this parallelepiped to the right and a force of equal strength will pull the bottom surface to the left. As the parallelepiped is supposed to consist of a fluid, it will be deformed under this stress. A certain velocity v will be imparted to the top with respect to the bottom. This velocity $v = \frac{dx}{dt}$ will be in direct proportion

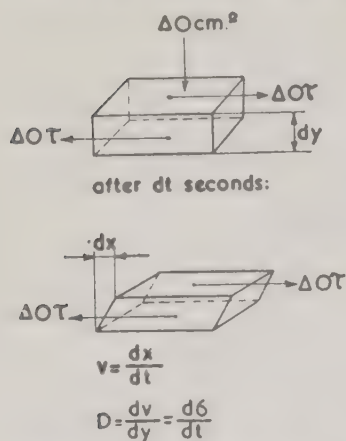


Fig. 8a. Deformation of small parallelepiped.

rate of flow). From Fig. 8b we derive:

$$D = \frac{dv}{dy} = \frac{d \frac{dx}{dt}}{dy} = \frac{d \frac{dx}{dy}}{dt} = \frac{dtg\sigma}{dt} \approx \frac{d\sigma}{dt}$$

for low rates of shear.

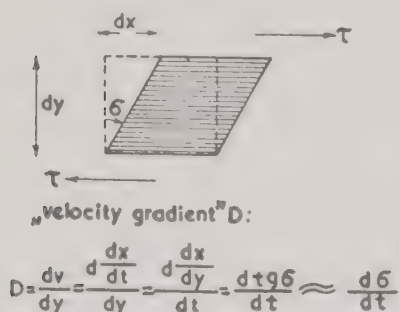


Fig. 8b. Derivation of formula for rate of shear D .

So NEWTON's law states that where there is homogeneous shear, the speed of deformation is strictly proportional to the applied force, viz.,

$$D = \frac{d\sigma}{dt} = \frac{\tau}{\eta}$$

η being the viscosity coefficient, $\frac{1}{\eta}$ the mobility.

From this law the flow of ordinary liquids through tubular canals is predictable, resulting in POISEUILLE's law; this

law is true only for speeds, not exceeding certain limits, depending on the fluidity of the liquids and the dimensions of the tube. Above these limits, the movement of the particles of the liquid will deviate from the direction in which the pressure diminishes. Turbulent flow will take the place of laminar flow. For our purpose, however, only the latter is of interest, and we shall ignore turbulent flow. Laminar flow can always be conceived as a movement of (extremely thin) layers, sliding one over the other.

NEWTON's law holds true for simple liquids. Liquids containing large

molecules or solid particles often do not follow this law. In many cases, however, a deviation from $D = \frac{\tau}{\eta}$ occurs only at low shearing stresses.

This can easily be understood in the case of liquids containing non-globular particles.

If the liquid is in slow motion, these particles will drift in random orientation. A strong movement will orientate them in the direction of flow, thereby diminishing the resistance which the particles exert to the applied force. Once this orientation is established, the fluid will follow NEWTON'S law at higher stresses¹.

What has been said here about deviations from the simple law

$$D = \frac{\tau}{\eta}$$

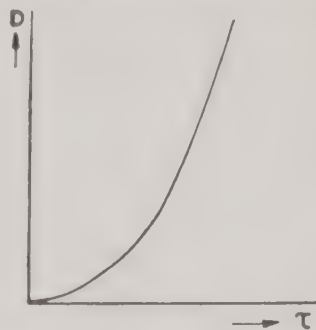
at low stresses applies not only to dispersions or colloidal solutions of rigid non-spherical particles, but also to dispersions, melts, or colloidal solutions, containing possibly globular, but deformable, particles or large deformable molecules (or clusters of chain molecules). Emulsions will show the same effect. Only in the case of suspensions, where the dispersed globular particles themselves are rigid, is orientation out of the question; the same is true for a melt containing globular rigid molecules*.

But the greater part of these suspensions containing *deformable particles*, especially if present in large concentrations, do show deviations from NEWTON'S law and not only at low stresses. For these cases, this law can be extended to

$$D = \frac{\tau^n}{\eta} \quad (2) \text{ See Fig. 9.}$$

It is not possible to say exactly what the meaning of the constant n is, in a physical sense; obviously it expresses the capacity of the particles to be deformed and (or) orientated³. With the proper choice of n , the law holds in quite a number of cases.

It is a different matter when a liquid or semi-liquid consists of a dispersion of largish particles in a liquid, with the



non-Newtonian or quasi-viscous liquid

$$D = \frac{\tau^n}{\eta}$$

Fig. 9. Rate of shear strain D as a function of stress τ for a non-Newtonian or quasi-viscous liquid.

* For the influence of the concentration on the viscosity of solutions containing large molecules, see².

particles touching one another and requiring a certain stressing force before sliding begins between the solid particles *. Quite possibly, the deformation of such a *plastic mass*, after this first limiting stress has been overcome, is governed by the viscous resistance to deformations, exerted by the liquid between the particles. NEWTON's law can be applied in these cases, if the limiting stress f , necessary to overcome the "dry" resistance between the solid particles, is subtracted from the total deforming stress τ . This is BINGHAM's law:

$$D = \frac{\tau - f}{\eta} \quad (3) \text{ See Fig. 10.}$$

It holds true, or almost so, for suspensions like certain clays in water and certain paints.

A combination of "dry friction" and "deformation of particles" occurs in many plastic mixes and can often be represented by DE WAELE-BINGHAM's law:

$$D = \frac{(\tau - f)^n}{\eta} \quad (4) \text{ See Fig. 11.}$$

As there are two constants in this formula, by proper choice it will be adaptable to many experimental results. The constant n seems to have a similar meaning as in eq. (2). The formula is useful for classification and description of rheological types. In practice it is often very difficult to decide whether a real yield value (f) exists, or whether permanent deformation already occurs at the smallest stress applied (if one waits long enough).

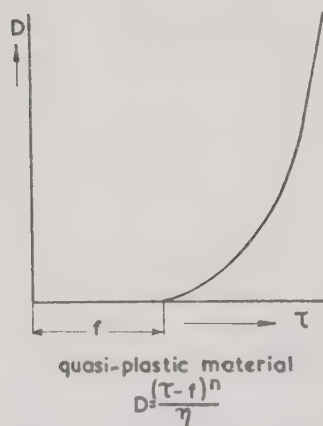


Fig. 11. Rate of shear strain D as a function of stress τ for a quasi-plastic material.

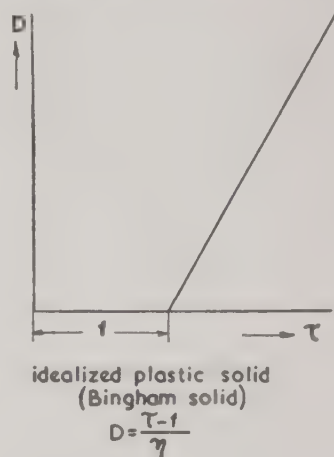


Fig. 10. Rate of shear strain D as a function of stress τ for an idealized plastic solid (BINGHAM solid).

The fundamental rheological formulae mentioned above represent the four main types of rheological behaviour. There are, however, some other rheological phenomena of great importance which are not so easily formulated. For, not only is $dD/d\tau$ dependent on the velocity of shear (in the case of non-Newtonian

* In cases of long-range forces between the particles this situation occurs, when the spheres of activity of these forces touch each other⁴.

liquids), but often depends on the duration of the shear as well. In many cases, this influence of the amount of shear on the resistance to further deformation is responsible for the remarkable effect the history of the sample previous to deformation has on its rheological behaviour. Such materials have a rheological memory. And in the second place, these materials often show a marked degree of "high elasticity".

High elasticity may be defined as the ability of a material to revert to its original shape in a pronounced degree after severe deformation (and not as the ability to stretch greatly before breaking). The possession of such elasticity enables it to recover (to a certain extent) after deformation. In most cases, this property will disappear if the material is kept in the deformed (*e.g.* stretched) condition for a long time.

Let us now examine the structure and properties of the materials, to see whether they can suggest some explanation of the complicated rheological behaviour we have been considering. Afterwards we shall describe the different forms of elastic-plastic behaviour, starting from these structures and properties.

Elastic-plastic substances always contain particles that are elastically deformable, *i.e.*, revert to their original form when the deforming stress ceases. These particles may be embedded in a (viscous) liquid and may consist of drops of a different liquid⁵ or of deformable clusters of big molecules. W. KUHN⁶ describes the exact thermodynamic reasons why such large molecules will recover their original shape after they have been deformed. If we have to do, not with particles embedded in a liquid, but with clusters of large molecules, these large molecules, when under a constant shearing stress, may be able to slide along each other. This is the case in a melt like rubber. In both cases the particles are deformed by a viscous flow of material along their surface. As soon as this flow or sliding ceases, that is, as soon as the deforming action stops, these drops or clusters of molecules tend to regain their original and most probable shape. They do so as a result of the elastic tension, set up in the deformed drops by the surface tension, which tends to make them round again; or, in the big molecules or clusters, by their tendency to return to their original shape. In re-assuming their original shape, the particles, in their turn, now strain the viscous material in a way that impels the whole body to revert to its former shape. If this body is not free to regain its shape, the big, strained molecules or drops will find other means of regaining their normal shape, moving and re-shaping themselves in their viscous envelope. This process of losing inner stress by slow movements of very tiny particles, or parts of the molecules, within the strained material is called relaxation.

Its effect on the rheology of plastic materials is rather complicated.

As this interpenetration of the elasticity and flow of substances in the plastic state is fundamental to the rheology of adhesives, we would do well to consider it in some detail, taking the different kinds of elasticity and their origin first.

The elasticity of materials like steel and rigid stones is a matter of very small deformations. Here the forces applied are found within limits to be directly proportional to the deformation:

$$\frac{dx}{dy} = \frac{\tau}{G}$$

In this equation ⁷ the coefficient G is the shear modulus of rigidity of the material considered. This is HOOKE's law.

This kind of elasticity, however, though truly shown by plastics in a very rigid state (*e.g.*, adhesives, which are hardened thoroughly), has very little in common with the elastic behaviour of concentrated solutions of high-molecular weight substances, of soft plastics, of bitumens, etc.

On the theoretical side, a big difference is indicated by the fact that the energy exerted by an elastic deformation is stored in quite different ways in the two cases. In rigid substances, following HOOKE's law, the deformation consists in a minute displacement of the elementary units of the substance with respect to each other. These elements may consist of ions (in metals and ionic crystals), of molecules (molecular crystals) or of atoms (rigid organic materials). Their distance is changed by the deformation; they have therefore moved out of their potential

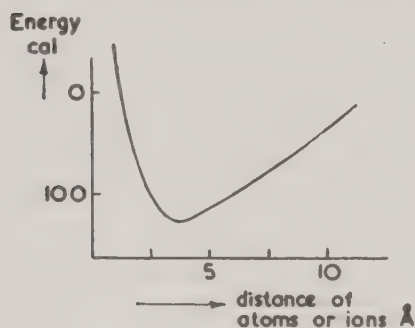


Fig. 12. Potential energy as a function of the distance of atoms. Curve for Na⁺ and Cl⁻ ions.

trough relatively to each other, and in so doing have gained a certain amount of potential energy. The source of the elastic tension in the material is very simple: it consists in the collective tendency of all elements of the strained structure to regain their normal mutual positions (distances). The effect of higher temperature will be a diminution of tension, because the increased thermal

movement of the particles will tend to enlarge the normal distance (see form of potential curve, Fig. 12).

In the case of high polymers in the elastic state, it has been proved that there is no increase of potential energy within the strained substance. ⁸

The amount of stretching may be 300 to 400% before an increase of potential energy sets in; the maximum amount of stretching may be as high as 1000% for rubber (see Fig. 13), against at most a few units per cent. in the case of metals. Further, HOOKE's law does not hold at all: the elongation depends

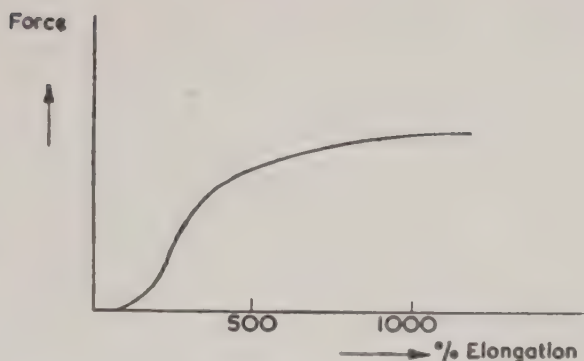


Fig. 13. Elongation curve of vulcanized rubber mix.

on the stress in a very complicated way⁹ and is only partly reversible in character. Part of the energy exerted, when rubber is considerably stretched, is consumed by frictional resistance in the material. But the perceptible evolution of heat, when a piece of vulcanised indiarubber is stretched quickly, has another source. When the stretched rubber is allowed to cool down to room temperature and is then released, it cools to below room temperature. This proves that it is not friction, but a mechanism comparable to the compression and expansion of gases which contributes to the evolution of heat during the deformation of a high polymer like rubber. Indeed, the elasticity of many high molecular weight substances (when stretched less than, say, 300%) may be explained rather by a kinetic play between parts of long chains. The elastic stress in these cases closely resembles gas pressure, which is known to result from the impact of many gas molecules in thermal motion. The elastic forces actuated in vulcanised and unvulcanised rubbers and polymeric plastics in the rubbery state, upon deformation, have an origin closely related to the chain structure of their molecules. This relation is not such that any mass built up of very long molecules must needs show great elasticity, or elastically reversible extensibility. But if such molecules show a certain mobility (which mostly occurs only within a certain range of temperature), they will show thermal motions preferentially perpendicular to their lengths (two-dimensional Brownian motion), because movements of atoms in the direction of main valencies demand more energy than those in a direction perpendicular to it.

If such a mass of vibrating chains (or of chains of vibrating and rotating chain-parts of spaghetti-like molecules) shows a chaotic (or no) orientation, however, this two-dimensional Brownian motion will not manifest itself in any way, because there is no direction of preference. On deformation, orientation occurs in the direction of flow, but if the molecules are free to

move, disorientation will follow again after some time (relaxation) due to the haphazard motions of the polymer-molecules. If, however, the chains are interlinked at not too many places, or if they are very much hindered from slipping along each other, orientation will be (semi-) permanent after deformation, and a two-dimensional pressure, perpendicular to the strain, will be set up. Since these materials can be looked upon as incompressible (except by crystallization, v.i.) an equal pull (negative pressure) originates in the direction of strain. Following this picture, one can see that the elastic tension in a stretched rubber is the consequence of kicks and pushes, originating from the thermal vibrations of chain-parts of orientated long molecules, these punches being distributed by every vibrating chain part to its neighbours. The force should therefore be proportional to the energy of vibration, that is, to the absolute temperature, which is exactly what MEYER and FERRI⁸ found.

Having discussed the mechanism of high elasticity at some length, we can now proceed to consider the rheological behaviour of materials containing highly elastic particles.

If such particles have restricted freedom to move past each other (it being irrelevant whether they are embedded in a liquid or surrounded in a melt by other molecules or clusters), the body as a whole will be elastic. After deformation it will recover its original shape. Such restricted freedom of movement can be established if only a few chemical bonds exist between different molecules in different clusters, of which vulcanisation in rubber provides a good example. It may also be that some long molecules extend from one cluster to another or that such molecules lie parallel over a limited part of their length, forming crystallites which also act as a bond between long molecules or clusters at a few points. Here raw rubber exemplifies the melt type; gelatine gels the embedded type*.

The elasticity of these materials is of a peculiar kind, because both the deformation and recovery are viscous phenomena: the clusters glide one over another, dissipating energy. The recovery is never instantaneous; the last part of the recovery, in particular, often taking hours or even days (slow elasticity).

As has been shown above, this kind of elastic stress increases with temperature; a stretched piece of material like rubber will increase its contracting stress when heated**.

But at the same time, viscous flow increases exponentially with temperature. Therefore, these materials are liable to be very elastic

* J. C. DERKSEN¹⁰ showed crystallites to be the binding agents in such gels.

** A heat engine on this principle was built by W. B. WIEGAND¹¹.

and quick at high, and very tough and slow at lower temperatures.

When drops, molecules or clusters are free to move in a viscous medium, we have a truly elastic-plastic substance. If the viscosity of the medium is very great (e.g. plasticised polyvinyl chloride), we find nearly the same behaviour as that characterising vulcanised high elastic polymers, except that recovery is imperfect. At low viscosity of the medium we get fluids which deviate from NEWTON's law, at least at low rates of shear. For the drops, molecules or clusters will be deformed by the shear and will recover at the same time, the actual deformation depending on the rate of shear. But the effect on rheology will be different here for the melt type and the embedded type of elastic plastic substance. In both cases the particles will be stretched, but in the first case this will result in an increased resistance to deformation, in the second case in decreased resistance. For the stretched particles of molecules in a melt will present a far larger surface towards each other, increasing the resistance to gliding, while the stretched particles in a medium will be at a greater distance from each other in a direction perpendicular to their length. The thicker layer of liquid between those particles will be easier to shear. The stretching of polythene* is a good example of the stiffening action, the behaviour of asphalts or nitrocellulose solutions of the decrease of viscosity at higher rates of shear.

In this latter case we shall find in the first place a heightened mobility during the beginning of deformation**.

During this period, part of the strain consists in the (highly) elastic but

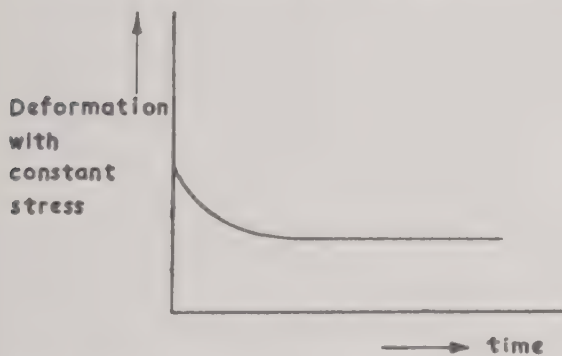


Fig. 14. Deformation of asphalts or nitrocellulose solutions with constant stress.

limited deformation of the individual particles, the rest of the strain being caused by the real (permanent) flow or limitless deformation of the substance between these particles. The very first deformation will occur within the deformable particles; the initial rate of shear, therefore, will be rather high. On further straining of the body consider-

ed, less and less elastic deformation of those particles will take place and

* The stiffening of polythene on stretching is, however, also a consequence of crystallisation which sets in after the orientation of the long paraffin molecules is effected by stretching.

** This increased deformation is almost the opposite of thixotropy (v.i.) and is different from dilatency (v.i.), because it does not lead to absolute stiffening.

more and more viscous straining of the substance between the particles; in the case of a melt, there is more and more viscous movement of these particles along each other. The picture of the beginning of such a deformation is as in Fig. 14.

When the deformation ceases, the deformed particles will have the tendency to return quickly to their normal form and/or position. But this tendency and the tensions that are its expression will diminish with time, if the body is hindered from moving back. If such outward movement is possible, it will be quick in the first moment and its rate will then decrease. For in the first moment, the elastically deformed particles will regain their normal shape, as far as possible (because of the resistance of their environment and neighbouring particles). For further recovery, viscous deformation of this environment is necessary, and this takes time.

Another rheological property of a very distinct character occurs in such (mostly micro-heterogeneous) materials, showing a very loose "structure" of a certain kind which builds up spontaneously, if the liquid or semi-liquid is left undisturbed. Solutions of gelatine, or suspensions of bentonite, provide good examples of these *thixotropic* systems. Such systems show high resistance to deformation (sometimes even a yield value) if they are in the undisturbed state; once a certain amount of deformation takes place, this resistance abates. In such a case the resistance to deformation (or the viscosity) is not in the first place dependent on the rate of shear, but on the previous history. If the material contains solid particles¹² (as in clays) *, the phenomena can be depicted as a temporary "sticking together" of these particles. When they touch each other at certain points, they stick. In this case, the liquid that surrounds the particles must be of such a kind as not to prevent direct contact between the particles; moreover, these have to exert mutually attractive force **.

* Where the particles exert long-range forces through the liquid, special forms of the potential curves may occur, hence the surfaces of the particles will tend to come to rest at specific distances, depending very much on the ionic content of the liquid. As HAMAKER (see HOUWINK, *l.c.*) has shown, these curves may show one or two minima or potential troughs, systems showing these potential curves being especially likely to show thixotropy. Whether thixotropy as shown by organic adhesives is to be explained along similar lines to those suggested for its occurrence in ionic systems containing ionising (high dielectric constant) liquids, the present authors would not dare say.

** This picture is rather crude. It is known, for instance, that in aqueous surroundings containing ions in a dissociating medium, the particles do not touch; they are surrounded by double layers. The potential curves here can be such that the surfaces approach each other to within a very short distance, coming to rest there in a "potential trough". This is the result of the interpenetration of the double layers of both surfaces. It results in a relatively rigid position of both particles with respect to each other. See HOUWINK's book, mentioned above¹².

In other words, the particles should not be too well solvated, not be dressed with a firmly adhering coat of adsorbed molecules of the liquid.

If the material contains no solid particles, but only large molecules (or clusters of these), the cohesion may be a local crystallisation of parts of several of these molecules. Here, too, a very thorough solvation may interfere with thixotropy. Often the phenomenon occurs only within a certain range of temperature. The system mostly shows a marked yield value; some authors even restrict the term thixotropy to systems with a yield value in the undisturbed state. However, this yield value disappears on stirring. It does not reappear at once after the movement has ceased, because the particles need time to find advantageous positions in which they can again cohere.

Thixotropy cannot satisfactorily be depicted in a graph, the system being irreversible. For systems, however, which are slow to pass from the disturbed to the "restful" state, one can determine stress/rate of strain curves at different intervals from the time of disturbance. Such curves, taken from the work of RÖDER¹³, are given in Fig. 15 for a 6.2% dispersion of bentonite and in Fig. 16 for a Fe_2O_3 "solution" containing 150 m mol KCl. Fig. 16, in particular, illustrates the building-up of the yield value.

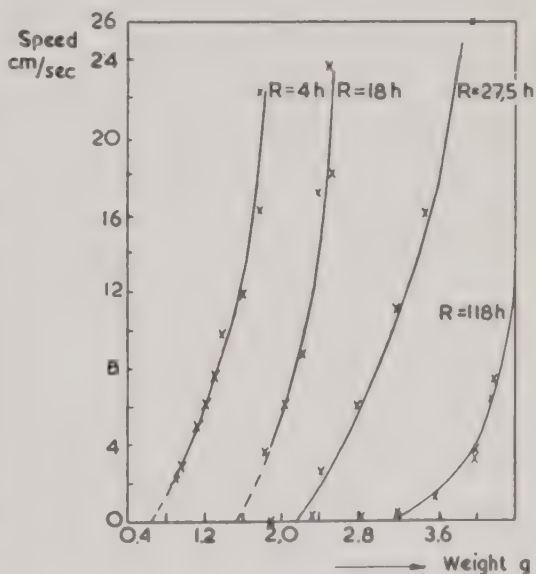
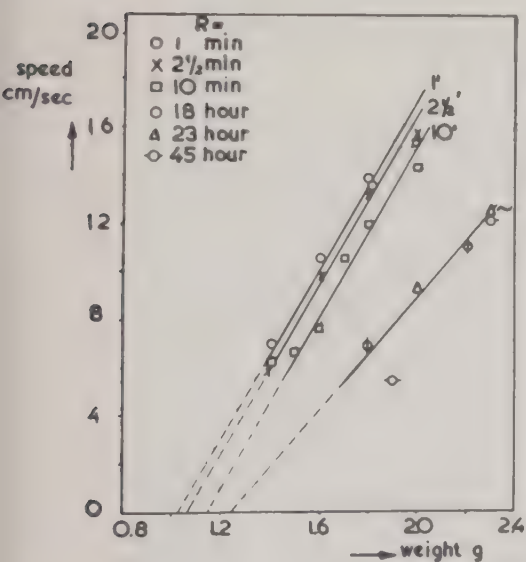


Fig. 15. Speed/weight curves of 6.2% dispersion of bentonite as function of the "time of rest" R .

From: H. L. RÖDER, *Thesis*, Amsterdam, 1939.

Fig. 16. Speed/weight curves of Fe_2O_3 - "solutions" as function of the "time of rest" R .

From: H. L. RÖDER, *Thesis*, Amsterdam, 1939.

The rheological changes which accompany thixotropic gelation are also shown by Figures 17 and 18¹⁴.

Fig. 17 shows a set of flow curves for a special bentonite suspension after different setting times. In this case, the completely agitated sol behaves essentially like a Newtonian fluid for small stresses. The gelation results in a decrease in slope of the D - τ curves and in the appearance of a yield value. D is the rate of flow or rate of shear strain $\frac{d\sigma}{dt}$, τ is the shear stress. In Fig. 18 a three-dimensional D - τ - t plot is given, where t represents the time of setting.

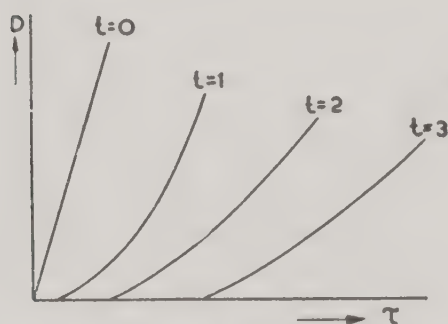


Fig. 17. Set of flow curves for a thixotropic material immediately after agitation and after various setting times.

From: TURNER ALFREY: *Mechanical Behaviour of High Polymers*.

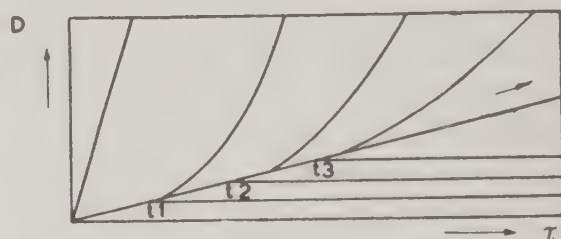


Fig. 18. Three-dimensional D - τ - t plot for a thixotropic material.

From: TURNER ALFREY: *Mechanical Behaviour of High Polymers*.

A third particular property, which occurs in a number of heterogeneous systems, is that of *dilatency*. In a certain sense it is the opposite of thixotropy. Dilatent systems are solid or highly viscous when stirred and fluid when undisturbed.

The behaviour of these systems is easily understood, when one thinks of a stable suspension with such large or heavy particles that it almost coagulates. To make a suspension stable, the particles must be coated with something that prevents actual contact between their rigid surfaces. In speaking of thixotropy, we have already mentioned such coatings; thixotropic suspensions being only relatively stable, we said that their particles should not be too firmly coated. In watery systems this coating mostly consists of an ionic swarm (double layer). The particles attract to their surface one particular kind of ions, and because of the very considerable electric charge of these ions, ions of the opposite charge preferentially gather in the fluid at a short distance around the charged particles (charged by the ions they attract).

These charged spheres around the particles repel each other and the particles therefore do not touch. These forces are highly dependent on the amounts and kinds of ions present; thus a situation may arise in which the particles can just be borne by their double layers.

A small additional mechanical force will overcome the forces between the outer shells of the double layers, making them interpenetrate, and establish mechanical contact between the particles. The effect will be a stiffening of the system, which was fluid when unstressed. This behaviour is called dilatency. Furthermore, if the particles are present in large concentrations and the system is left undisturbed, they will find their most advantageous position of close packing when shielded by their double layers. When stirred, however, the relative position of the particles will be disturbed. They will touch each other and, because of the great frictional resistance caused by their immediate contact, the closest packing will be lost and the volume in the interstices between particles will increase. The total volume of these interstices is quite liable to exceed the volume of the liquid present. In this case, a fluid system will become exceedingly dry and brittle as the result of stirring, and this lack of liquid will induce strong negative pressure, causing the particles to be drawn together by suction. Left to itself, the system "melts" again in a few moments and is as fluid as it was before. This is what one sees with drifts of sand (quicksand) and with, say, a mixture of potato-flour and water. The phenomena of dilatency are not of great importance to the rheology of adhesives, but are included in this superficial review of rheology because of their instructive character.

§ 2. RHEOLOGY OF ADHESIVES BEFORE AND DURING HARDENING

Application of an adhesive and gluing can be divided into the following stages:

- (1) A liquid adhesive (sometimes it is a powder which is afterwards converted into a liquid) is applied to a surface.
- (2) The liquid adhesive layer is converted into a viscous form.
- (3) Two surfaces are joined (tackiness).
- (4) The layers are converted into solids or into highly viscous liquids (or into the plastic or highly elastic state).

Stage (2) of this scheme is sometimes omitted, (3) and (4) being often united into one stage. Sometimes stage (4) is omitted (permanently tacky adhesives).

We shall also have to speak of several combinations of the stages, in which the adhesive layers are liquefied, united, solidified, etc.

(2) Application of (liquid) Adhesive

As described elsewhere in this book, in most cases adhesives should form a very thin, but continuous layer in the joint on account of the mechanical and rheological properties of the hardened layers of adhesive. We shall revert to this point in § 3 of this Chapter, but the actualisation of these thin adhesive layers in the joint depends largely on the rheology of the adhesives before and during the hardening.

It is not enough to apply the adhesive in a thin layer; this layer has to stay in place during the following stages and eventually has to resist the relative motion of the solid surfaces which it joins. It is always necessary that an adhesive should wet the surfaces which have to be bonded, otherwise good adhesion is out of the question. For, in the first place, a wetting adhesive spreads over the solid surface, thus facilitating application in a thin layer. Secondly, if the adhesive wets the solid, it shows that molecular forces of attraction are acting on the molecules of the solid surface, which attraction is necessary for a good adhesive joint. In order to wet a smooth solid surface, the liquid adhesive, when applied, must exhibit a low contact angle on the solid surface. The contact angle is the angle at which the boundary of the liquid adhesive meets the solid surface. If the attraction between solid and liquid is equal to, or in excess of, the cohesive forces of the liquid, the contact angle will be low or zero and the liquid will spread. If the attraction of the liquid molecules by the solid is weak and, there being a strong mutual attraction between the molecules of the liquid, the contact angle is large, no wetting occurs, but droplets of adhesive will be formed on the solid surface. Drop formation causes poor contact between solid and adhesive and a small interfacial area where the forces of attraction can work, resulting in a poor adhesive joint. A low surface tension of the liquid adhesive is one of the factors which are favourable for spreading. Other factors influencing wetting are the viscosity of the adhesive and the nature and condition of the solid surface. It is possible to modify the properties of the liquid-solid surface by adsorbing suitable substances on the solid. These "surface active agents", dissolved in the liquid adhesive, form an adsorbed film on the solid, which is of considerable influence on the wetting properties of the liquid adhesive.

If we have not to do with a smooth surface of the adherend, but with a rough or porous one, wetting is still important. For, if the liquid adhesive enters cavities and pores of the solid surface and wets their inner walls, the actual area of the joined surfaces is very much increased. In so far as this increase of mutual surface is obtained, a limited "penetration" of the liquid

adhesive into a porous adherend is to be regarded as a favourable circumstance. On the other hand, much experimental work has shown that excessive penetration should be avoided, for it may cause a broken glue line and a poor joint. In finding the best rheological method for the application of an adhesive, some understanding of the nature of adhesion has proved to be desirable.

In studying the nature of adhesion, much work was done in Great Britain by J. W. McBAIN and his co-workers, published in the three Reports of the Adhesive Research Committee, and in the United States by F. L. BROWNE and T. R. TRUAX of the Forest Products Laboratory.

McBAIN distinguished between *specific adhesion*, caused by molecular attraction with smooth, dense surfaces, like polished metals or crystal surfaces, and *mechanical adhesion*, caused by mechanical grip action or interlocking of the set adhesive in the surface irregularities, cavities or pores of a rough surface of the solid adherend, as in the case of wood, cloth, ceramics.

McBAIN first supposed the gluing of wood to be essentially of a mechanical nature. In this mechanical conception it is assumed that the glue is forced into the pores of the wood surface by exterior pressure and hardens in the form of projections and tentacles in the pores. The strength of the joint is due to the resistance with which these projections oppose the action of a shearing force. This mechanical view of the nature of wood gluing, which was afterwards shown to be unlikely, led to false methods in the plywood fabrication process. The "heat, hurry and squeeze" method, resulting from this mechanical view, used a very thin fluid adhesive and a substantial pressure was applied at a rather high temperature. This led to an excessive penetration and squeezing out of the glue between the solid surfaces, resulting in a "starved joint" with a broken glue line. The starved joint proved to be a joint of inferior quality*.

The experimental work of F. L. BROWNE and T. R. TRUAX¹⁵ made evident that, in the gluing of porous materials, such as wood, adhesion is to a high degree specific and not simply mechanical. Here, too, molecular forces play an important part. This was shown by mechanical tests and also by microscopic examination of the glue penetrated into the wood pores*.

After shrinking of the glue in the pores by drying, it still adheres to the walls of the pores, leaving a thin layer and forming a hollow cylinder, sticking to the walls**.

* See Chapter 5 A of this book by E. D. CORNWELL.

** See microphotographs in Chapter 5 A of this book by E. D. CORNWELL.

So, wetting of the inner walls of the pores and specific adhesion to the wood are evident. The effective area of the adherent surface is much increased by this behaviour of adherend and adhesive. The conclusions of BROWNE and TRUAX were as follows:

- (1) For strong wood joints an observable, continuous, adhesive film is necessary;
- (2) There is no correlation between strength of the joint and the amount or depth of penetration of glue into the vessels or luminae of the wood, provided sufficient glue is left in the joint to give a continuous film.

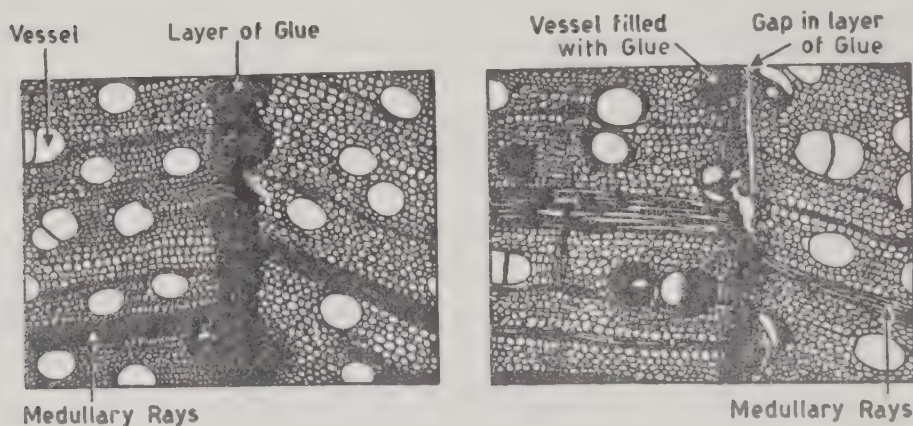


Fig. 19. Photomicrograph of sections through wood joints showing a good joint (left) with a continuous glue layer and a starved joint (right) with a broken glue line.

From: F. L. BROWNE and T. R. TRUAX, *Ind Eng. Chem.*, 23 (1931) 290.

The two pictures of Figure 19, taken from the publications of BROWNE and TRUAX, illustrate the continuous glue film, being the chief condition for a good joint.

BROWNE and TRUAX investigated animal glue wood joints, but their general conclusions are useful for other adhesives as well, e.g. for synthetic resin glues. This is shown by the work of J. W. MAXWELL¹⁶, who determined the types of surface, and the exterior pressures which gave the strongest joints in plywood manufacture with resinous glue. His results are a confirmation of the general ideas propounded by BROWNE and TRUAX. So are those of FARROW, HAMLEY and SMITH¹⁷, who removed the wood of phenolic resin glued wood joints by digestion with chromic acid, and studied microscopically the resin glue which was left. Their main conclusion is: "In a good wood joint the wood tracheae are just wetted, leaving thin-walled resin tubes. The resin penetrates just below the surface as it

is left by the cutting tool". From the work mentioned above it is shown that our main objectives in gluing are the following:

A continuous glue line, essential for a good joint, must be obtained. The glue must wet the surfaces and must be brought into contact with all parts of the surfaces.

Penetration, so far as it wets pores and cavities, thus increasing the effective surface area, is desirable, but excessive penetration and squeezing out of adhesive must be avoided.

To fulfil the latter conditions, a suitable balance must be maintained between the pressure on the joint and the consistency of the adhesive at the time of pressing.

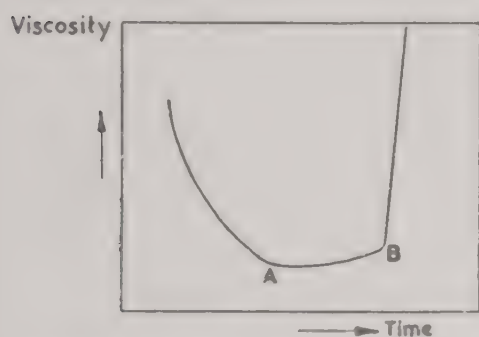


Fig. 20. Viscosity of special Aerolite resin glue during hot pressing of plywood.

From: Aero Research Technical Notes Bulletin No. 7 (July 1943).

How this is achieved is shown clearly by the graph of Fig. 20¹⁸. The graph shows the variation of the viscosity of a special Aerolite glue and hardener mixing during hot pressing of plywood veneers. During the first phase of the gluing process, the glue in the joint is heated and consequently the viscosity decreases to point *A*. Meanwhile loading of the press has begun. From time point *A* the temperature reaches a level at which the glue begins to thicken, due to the action of the hardener and other

materials of the glue. The viscosity remains almost constant for a while. During this time a moderate pressure is maintained. In the final stage, starting from *B*, the liquid adhesive is changed first to a gel and finally to a solid by polymerisation. Within this setting time the viscosity increases rapidly; and from point *B* the loading pressure can be gradually brought to its maximum value. After the complete setting of the glue, the pressure is released and the panel removed from the press.

If the surfaces to which the glue adheres are rough, as is often the case with wood, a layer of glue of appreciable thickness is necessary to give a continuous adhesive layer. Between smooth non-porous solids, the layer of adhesive can and must be exceedingly thin for giving the strongest joints.

It was necessary for us to give this rather elaborate survey of the work done to elucidate the importance of specific adhesion versus mechanical interlocking of adhesives on wood, because the technique employed for

the application of adhesives to wood depends on it. As we know that the interfacial forces between the sound wood surface and the glue are the prime factor, we have to apply the adhesive in a way that will establish perfect contact between the two (see the next paragraph and the chapter on adhesion). From our rheological point of view, we must apply it, not as a dough under high pressure, but in a perfectly fluid state, so that it may flow freely over the surface.

The application of thin layers calls for thin fluids; on the other hand a viscous fluid will tend less to be sucked away into pores before the setting transforms it into the solid (plastic), highly viscous or highly elastic state. The adhesive is, therefore, often applied in solution, in the hot state or admixed with a powder (flour, wood meal), the latter having a tendency to retain the adhesive. Rheologically, a thixotropic adhesive would seem to be the best answer to the contradictory conditions of a fluid adhesive during application and a viscous adhesive during (hot) pressing. Such fluids are the well-known bentonite-asphaltic suspensions used in surface coating and as an adhesive. Hitherto thixotropic methods have apparently been rare in practice, and even for asphaltic emulsions thixotropy is combined with the use of a liquid (water) that dries out after the adhesive has been applied. Thixotropy does, however, play a part in the production of special adhesive compositions used in fibreboard manufacture. Superior rheological properties of these adhesive compositions are characterised by a yield point value and a "thixotropic ratio". See p. 71.

Animal glue (see Chapter 5A by E. D. CORNWELL) is a very good example of an adhesive which, applied as a fluid, afterwards spontaneously becomes highly viscous or even solid; these glues are always applied as hot solutions, gelating by virtue of the colloidal properties of gelatine and animal glue. Gelation sets in a short time after the glue has cooled down to room temperature, forming a sticky semi-solid with a pronounced yield value. Afterwards this gel dries out; in this case the drying-out is not the transformation of the applied adhesive layer from the liquid to the highly viscous form, but the setting of the adhesive layer. Thixotropy comes into play in the first part of the process: gelatine and glue solutions, within a certain range of concentration, when cooled to temperatures well under their gelation point, show thixotropy very clearly.

The gelation of gelatine solutions is in itself a very complicated process. This is shown by the following data¹⁹:

Hot gelatine solutions of 2, $1\frac{1}{2}$, 1 and $\frac{3}{4}$ % were divided into two parts each, one part kept at 20° C, the other part at 2° C for 14 days. In Table 8 the occurrence of gelation is marked by +:

TABLE 8

GELATION OF GELATINE SOLUTIONS

Conc.	Days at 20°										Days at 2°									
	1	2	3	4	5	6	7	8	14	1	2	3	4	5	6	7	8	14		
2 %	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
1½ %			+	+	+	+	+	+	+											
1 %				+	+	+	+	+	+											
½ %																				

The reason of this behaviour lies in the fact that the gelation is caused by some sort of crystallisation in the gelatine. The rate of this crystallisation is very low at low temperatures. But the use of glue could only be classed among the thixotropic methods if the gelated solution, being stirred at room temperature (till it was fluid) and then being applied, the gluing process were effected after this applied fluid had gelated again. As in reality the change of temperature is of prime importance, thixotropy plays only an accessory part.

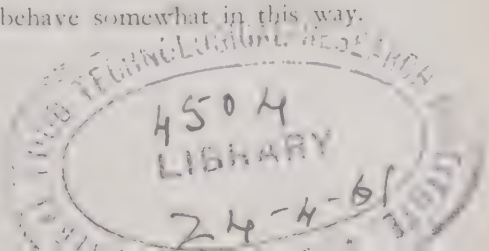
This complicated rheological behaviour of “glue” accounts for its usefulness in carpentry and furniture joining. Thanks to the sudden conversion from the liquid to the sticky, plastic state, the pieces can be placed in the right relative position, with a fluid layer in between; after a very short time, the glue will have cooled and the pieces will stick together. Simple viscous solutions never behave like this, a prolonged period being required before the liquid reaches the sticky state by a process of evaporation or diffusion of the solvent or by a chemical process. No gelating plastic adhesive is known to the present writers, but any such would probably find widespread application. *

It depends upon this same conversion period from the liquid to the highly viscous state, whether an adhesive is called “long” or “short”.

These remarks, however, refer to a stage beyond the actual application of the glue and we shall revert to them as well as to the question of tackiness when dealing with the joining together of the surfaces to which an adhesive has been applied.

Some adhesives are not applied in the fluid state, but, *e.g.*, as a powder or as a solid film. Of course, in these cases, the application involves no rheological problems.

* Organosols like those of cellulose acetate-butyrate, behave somewhat in this way.
References p. 88



(b) *Conversion of a liquid Adhesive into a Highly Viscous Form*

The drying out of a dissolved adhesive is not a very simple process. If a viscous lacquer solution or a dissolved adhesive is spread out over a plane surface without any loss of solvent * and if the loss of weight is then recorded during the evaporation of the solvent, the result is in accordance with the well-known evaporation rates of solvents. The rate of evaporation of solvents from the solutions, as compared with that of pure solvent, however, is found to be decreased in different degrees by the specific retaining power of the body dissolved. If, however, a small percentage of a solvent of lower vapour tension is present, the whole evaporation curve drops to a considerable extent. This decrease in rate of evaporation starts almost from the beginning of the drying process, due to the fact that the solvent diffuses through the layer of viscous material and partly evaporates at the surface. The solvent remaining at this surface will gradually become enriched by the high-boiling component. This process goes on until the evaporation rate is almost as low as that of the high-boiling component. In evaporation experiments with solvents and solvent mixtures without a solute, this effect is not found, because the upper layer, where the slowly evaporating solvent tends to be concentrated, continuously sinks back into the liquid.

Adhesives of the air-drying type often contain plasticizers which will act in the same way as high-boiling solvents. Presumably such plasticizers are brought to, and concentrated in, the surface during the evaporation. ** A second effect, the retention of solvent by high polymers, is often very stubborn. Chlorinated rubber, for example, often contains 10% or more of carbon tetrachloride; even if the material is in a finely divided state, this solvent cannot be eliminated at 100° C in an oven. The only way is by dissolving and precipitating from this solution by means of a non-solvent. The rheology of adhesives is radically influenced by solvents thus retained. They act as a very effective plasticizer (because of their small molecules and low viscosity ²⁰).

In highly elastic adhesives, this plasticizing will induce enhanced elastic deformability or even a lowered yield value and, therefore, a plastic deformation. If the adhesive is normally in the highly viscous state, a retained solvent will lower the viscosity. These actions, however, are not permanent, because the solvents eventually evaporate or diffuse. A joint that seems

* One of the present authors performed this in an atmosphere saturated with vapour of the same solvent.

** The present authors do not know of any experimental confirmation of this effect.

strong and flexible shortly after it has been made, may become brittle and unreliable in this way.

Of great importance in this respect is the question whether the solvent is able to diffuse through the bodies that are to be joined. In joining polyvinyl chloride (p.v.c.), a solution of chlorinated polyvinyl chloride (German: "Nachchloriertes Polyvinylchlorid") is often used as an adhesive. This product dissolves in many solvents, whereas polyvinyl chloride itself is only soluble in special solvents like methylene chloride, cyclohexanone, methyl cyclohexanone. If p.v.c. parts are to be joined, however, the solvents for the chlorinated adhesive should contain a considerable amount of one of these solvents for p.v.c., otherwise the solvent retained by the adhesive will not diffuse through the p.v.c. *.

We have here confined ourselves to the rheological aspects of solvents in adhesive layers; but, apart from rheology, the presence of these solvents undoubtedly affects the degree of adhesion between adhesive and surface. We must now briefly consider this aspect, not only so that we may realize that it is fundamentally a matter of adhesion and not of rheology, but also to show that, in our view, micro-rheology is nevertheless involved in a certain sense. When a solution of some high molecular weight substance is applied to a surface, this surface will be wetted. By what? We think: essentially by the solvent **.

TABLE 9

LACQUERS OF DIFFERENT CONCENTRATION IN A SOLVENT MIXTURE OF PETROLEUM AND TURPENTINE (6 units vol. to 1 unit vol.)

Percentage of lacquer substance (drying oil + resin)	Surface tension dyne/cm
86	32.4
65	29.0
48	27.7
38	26.7
0	25.6

Note: The surface tensions of the 86 % and 65 % lacquers, as measured, will be somewhat too high. The lacquers in these cases form a highly viscous mass, which is the cause of uncertainties in the measurements.

* An adhesive used for this purpose by I. G. Farben is, for instance, chlorinated polyvinyl chloride 12%, acetone 5–10%, trichloroethanol 50%, remainder methylene chloride.

** This view is also strengthened by the fact that the surface tension of lacquers is in practice the same as that of the solvents used (see Tables 9 and 10).

TABLE 10
SURFACE TENSION OF VARIOUS SOLVENTS AND LACQUERS MADE WITH THEM

Name of solvent	Surface tension of pure solvent	Surface tension of 47 % lacquer substance in 10 % solvent + 43 % petroleum	Surface tension of 47 % lacquer substance in 53 % solvent
Butanol	24.4	26.8	
Cyclohexanol	34.4	27.3	33.0
Butylglycol	28.2	27.3	29.2
Ethyl glycol acetate	29.8	27.0	29.7
Cyclohexyl acetate	31.7	27.3	31.6
Cyclohexanone	34.7	27.9	33.7
Dioxane	33.5	27.4	31.6
Turpentine-petroleum (mixture 1 : 6)	26.6	27.2	27.2

The fourth column of this table shows that a lacquer with 47 % lacquer substance and 53 % solvent has a surface tension which is virtually the same as that of the solvent alone.

Only if very strong attraction between the surface and the molecules of the adhesive exists (for instance, between certain isocyanates and textiles *) can strong adsorption of the large molecules from the solution on the surface be expected. Even so, however, the dissolved molecules will not take up those positions relative to the solid surface which would guarantee the most perfect bond between adhesive and surface. Solvent molecules will lie at many places between the adhesive molecules and the surface. The adhesive molecules will not turn their most active points towards the surface, because these points (dipoles, for instance) will probably be preferentially occupied by solvent molecules. When the solvent afterwards diffuses away and evaporates, viscosity in the adhesive will rise and the micro-rheological act of the turning of the adhesive molecules with their active groups towards the solid surface will become less and less probable. As the last solvent molecules disappear (by diffusion) from between the adhesive and the solid wall, open spaces will be formed and no great adhesion can be expected. Only when the temperature is raised to a point at which free movement of the adhesive molecules begins, will there be improved adhesion. This is why air-drying lacquers always show a much lower adhesion than baked lacquers **.

* The Germans used "Desmodur R", a product of tris(*p*-aminophenyl)methane and phosgene, to bond rubber to textile-cord ²¹.

** This need for reaching a temperature at which free movement of the molecules is possible is very pronounced with lacquers of the vinyl chloride vinyl acetate co-polymer type; here, it is absolutely essential to raise coats of lacquer applied to metals to 160° C in order to establish adequate adhesion ²².

Evaporation of solvent is by no means the only way by which the applied adhesive is converted into a more solid state. Often (solder, asphaltic bitumens, sealing wax) a molten substance is applied and congeals. The peculiar behaviour of protein glues has already been mentioned.

(c) Joining the Parts

The joining of the parts after the adhesive has been applied and begins to congeal introduces the question of tackiness. Tackiness is commonly considered to be a rheological phenomenon. The term "tackiness" as used in different fields of industrial application carries different implications. In adhesive work tackiness is a pressure-sensitive adhesion and the cause of the resistance opposed to forces intended to separate two solids joined by an adhesive in the fluid state. The separating forces may pull in a sense normal to the adhesive layer, but tangential forces causing a shear of the fluid layer have also to be considered.

It is very difficult to define tackiness accurately. The whole phenomenon is not yet fully understood, nor is it known by what physical properties it is caused. Tackiness or stickiness is a complex property, a combination of a number of different simpler properties. Some of the contributive causes of tackiness are adhesion, cohesion, surface tension, viscosity, yield value. Tackiness is not a sum of these; the relationship is more complicated.

The tackiness of a material is often judged subjectively by a finger test in which the finger is placed on the tacky material, firmly pressed into it, and then abruptly lifted. If the material is tacky, the withdrawal of the finger will be impeded by forces within the tacky material acting in an opposite direction. We feel that the lifting of the finger requires appreciable exertion and even more to detach it from the material. If the tacky material adheres to the finger sufficiently, a film of it is left on the finger after its withdrawal. Here the work done was necessary to split the adhesive material, but the pulling forces are not always powerful enough to detach it. The opposing forces, resisting the flow or shear of the liquid adhesive, have then sufficient strength to hinder substantial relative movements of the joined parts. In many cases the tacky adhesive, first being in the liquid or soft plastic state, later solidifies and the joint is able to withstand fairly high loads.

Tackiness as a property of adhesive material is indispensable in various industrial applications as well as in everyday life. Thus instantaneous adhesion is required of adhesives used in the paper-converting industries making paper cartons, packing material (gummed tape), corrugated fibre

board, etc. What should we do if the adhesive gum of postage stamps and envelopes did not stick instantaneously to paper, owing to tackiness?

In boot and shoe manufacture tacky adhesives are necessary to maintain rate of production. We make use of the tackiness of natural unvulcanized rubber in repairing rubber tubes, using a rubber cement. This cement is a solution of unvulcanized rubber in a volatile solvent, mostly benzene. A thin layer of the rubber solution applied to the cleaned tube and to the patch leaves a thin, very tacky rubber film after evaporation of the solvent. In fixing the patch to the tube, a slight pressure is sufficient to join the rubber films and the join proves to be very durable. In World War II the lack of tackiness of synthetic GR-S-rubber caused a great deal of trouble and made it clear that the tackiness of natural rubber as used before was one of its most useful features, especially in building up tyres previous to vulcanization.

Many adhesives show tackiness as long as they are in a mobile, e.g. liquid, state and eventually, when they have solidified, lose their tack and give a rigid join. Some of them, however, remain in their original fluid state, in which case they are said to be "permanently tacky". Examples of this type are adhesive tape and surgery plaster. The advantage of these special types of adhesive is that they may be detached and removed without much trouble at any time.

We have stated before that the definition of tack is very confused. Even the conception of tack is not the same in the various branches of industry and it differs with the substances used. The tackiness required for adhesives is something different from that required in printing ink and the tackiness necessary in the rubber industry is not synonymous with the stickiness of adhesives, nor with the tack of printing ink.

Let us consider in detail the particular requirements for tackiness in those special cases, for an understanding of them will be very instructive.

What is called *tackiness in the rubber industry* is a property demonstrated to a high degree by natural unvulcanized rubber. Tackiness in this respect means that natural rubber does not stick to other materials, it is a non-adhesive, but it sticks to itself under slight pressure. ZHUKOV and THALMUD²³ call this property, which is typical of unvulcanized natural rubber, "autohesion". A property of GR-S-rubber and of reclaimed natural rubber is that it is a non-adhesive and has a total lack of autohesion as well. And precisely this lack of autohesive properties caused the trouble in the manufacture of rubber tyres from GR-S in the United States during the last war. In making tyres or other articles, several layers of rubber and layers of rubber-coated fabric or some other reinforcement coated with

rubber are applied. It is essential for the ultimate quality of the article that these rubber layers should stick together and unite, before the whole is vulcanized by heat and pressure. Much work was done to improve the tackiness and to give autohesion to GR-S rubber. The addition of extremely tacky materials, such as polyvinyl ethers, did not produce the desired effect. The addition of rosin had a peculiar effect, *viz.*, the GR-S rubber grew sticky, it showed adhesiveness to other materials, but did not stick to itself; it was not autohesive. As, after the war, the United States acquired the tackifier Koresin, developed in Germany to be used for synthetic Buna rubber²⁴, it was tried out as an improver of the tackiness of GR-S and proved to be a great success. Upon the addition of Koresin in proper quantities, the autohesive tackiness of GR-S approaches that of natural rubber.

J. R. SCOTT²⁵, in discussing autohesion, distinguishes two phases in the joining of two tacky rubber surfaces. His views are the following: The first phase is getting the two surfaces into complete and intimate contact. Before a good bond may be effected, the surfaces must be levelled by local flow of the material in order that they can make contact over the whole area. So a material must flow readily under small stresses if it is to possess "tack" as the rubber technologist understands the term. This is just the opposite of the requirements desired for a good adhesive between two adherends. For indeed, precisely those factors (yield value and high effective viscosity) which increase in this case resistance to separation and help adhesion, would resist the flattening of surfaces, which is necessary for autohesion. This agrees with the observation that GR-S flows much less readily than natural rubber under small stresses.

The second phase is mutual fusion of the surface layers. This, for rubber-like polymers, involves an interpenetration of the chain molecules composing the two surface layers; in the ideal case these become so thoroughly interlocked that there is no discontinuity in molecular structure at the junction plane, *i.e.* the bond is as strong as the mass. This implies rapid self-diffusion or ability of the molecules to slip readily past one another. This is closely related to, but not necessarily identical with, the easy flow under small stresses needed for the first phase.

Secondly, let us see *what the printer means by tackiness*. Printing ink is mostly a suspension of a coloured or black pigment in an oil-based or resinous binder or vehicle. Alternatively, solutions of resinous binders in organic solvents, coloured by aniline dyes, are used. The viscosity of these inks may be of the order of a few hundred poises. They behave like adhesives. It is interesting, therefore, to consider what happens with the thin layer of printing ink trapped between type face and paper during the printing process.

Here "tack" is the resistance put up when the type is separated from the paper after the print impression, resulting in a thin layer of ink being left on the paper and on the type. Tack of printing ink is caused by the forces resisting the splitting of the ink layer.

It is obvious that the tack of printing ink must be properly adjusted. When the ink is too tacky, "picking" occurs and the paper is damaged because some of its surface is pulled off.

If we try to discover how the splitting of the ink layer occurs, we may follow the views of H. GREEN²⁶. He says it is not likely that ink splitting will take place abruptly, for then the forces necessary to break the film against its cohesive forces (tensile strength) would be extremely large. It is more likely that the ink will follow the path of least resistance, will flow and "neck down" to thin threads, which are finally ruptured by relatively weak forces. So the tack of printing ink is a pull resistance, which is maximum at the start of the separating motion and is much less at the point of rupture. Pull resistance is caused by the *flow-resisting properties* of the ink, yield value and viscosity, influenced to a certain extent by the surface tension. The relative importance of these three properties can be determined only by experiment. Cohesion of the ink seems to be of negligible importance, as at the moment of rupture only thin threads, with a small transverse section, are broken, and the work done against the forces of cohesion is very small.

GREEN's explanation of the splitting phenomena: viscous flow and necking down into threads, will hold for a fairly slow or moderately fast separation of the liquid film. However, when the separation is very quick, the liquid film may be split by rupture in the pattern of a solid (see Fig. 21). This splitting by rupture is promoted by a high viscosity of the liquid, a high rate of separation, and a very thin film. The last factor is emphasized by J. BUCK²⁷, who claims that very thin layers of ink will rupture rather than



Fig. 21. Rupture pattern of adhesive film at very fast separation without laminar flow. From: Aero Research Technical Notes Bulletin No. 24 (Dec. 1944).

neck down, and that films of less than 10 microns' thickness behave differently from thicker ones. H. GREEN²⁶ does not agree with BECK in this respect and says that there is neither theoretical reason, nor experimental proof that layers of printing ink, applied in a film thickness of 2 to 6 microns, should behave in any abnormal manner, differently from films of 25 to 250 microns or more. Only if the film becomes extremely thin, say several molecules thick, GREEN expects abnormal flow behaviour, resulting in high flow resistance and then rupture of the film.

GREEN's views on the behaviour of very thin films are contradicted and BECK's experimental results are explained by F. A. ASKEW²⁸. The latter emphasizes the great importance of the *time factor* in the printing process and has the following suggestion: "The essential difference between the two aspects of printing ink tack: viscous flow, followed by necking down, on one side, and abrupt rupture, on the other side, depends on the time factor and is in some respects analogous to the difference between a force and a blow.

The concept of tack in the printing process includes essentially the rapid separation of two surfaces, both of them wetted by a fluid. This separation may take place by the rotation of rollers, or by finger-dabbing, but the times involved are small fractions of a second. If the fluid film separating the two surfaces is very thin, the gap available for the flow of fluid is at first very small, and a considerable force is necessary to overcome the viscous resistance. This view is in accordance with experience in the finger-dabbing test on these materials, which is that thin films of the same fluid appear more tacky than thick films. The faster the separation takes place, the greater the force necessary, and a stage will be reached at which the work required to be done in transferring the liquid against viscous forces would be greater than the work required to form two fresh air-fluid interfaces (*work of cohesion*)."

It can be calculated that for films of the order of 0.01 cm thickness and a fluid having a Newtonian viscosity of 100 poises, the film will split, if the separation is carried out in a time shorter than 1 second, and will be drawn up into a thread if the time is longer.

Definite indications for the existence of ink film rupture in newspaper printing practice are reported by A. VOER²⁹. The speed of separation here is so high, that the ink behaves purely elastically.

Finally we shall consider a *tacky adhesive*, for instance a liquid, between two solid adherent surfaces. First, there must be wetting of the solids by the liquid and adhesion between solids and adhesive. Normally, the fluid adhesive between the solids, though thin, will have a finite thickness and

the distance between the two solids will not be such as to induce mutual attraction between molecules of the two solids or even effect contact. Nor is it likely that adhesive forces will act through the adhesive film; rather will they work only at the interface between adhesive and solid. It is not likely that molecular attraction of the solids will reach beyond a monomolecular layer of the liquid adhesive. So the strength of the adhesive joint is determined in the first place by the behaviour of the adhesive. The tackiness of the adhesive will resist relative movements of the adherends, both in normal and tangential directions, if these movements are not too slow. In doing so, the tacky liquid fulfils the function required of an adhesive in general. If a separating force that is not too strong is applied to the adherends, and the time of application is not unduly short, no rupture will take place, but the liquid adhesive will show resistance to flow as well as to shear and to deformation, all of which counteract and balance the separating forces.

In practice the adhesives used are non-Newtonian and differ in rheological properties from Newtonian liquids, *e.g.* they have a yield value, are thixotropic, or are plastic-elastic. As there is no fundamental difference between a fluid tacky adhesive and a printing-ink, all that has been said about the rheology of printing-inks is applicable to adhesives, so long as the latter are in the fluid state. As we have seen, the time during which a pulling load, trying to separate a fluid adhesive between two solid adherends,

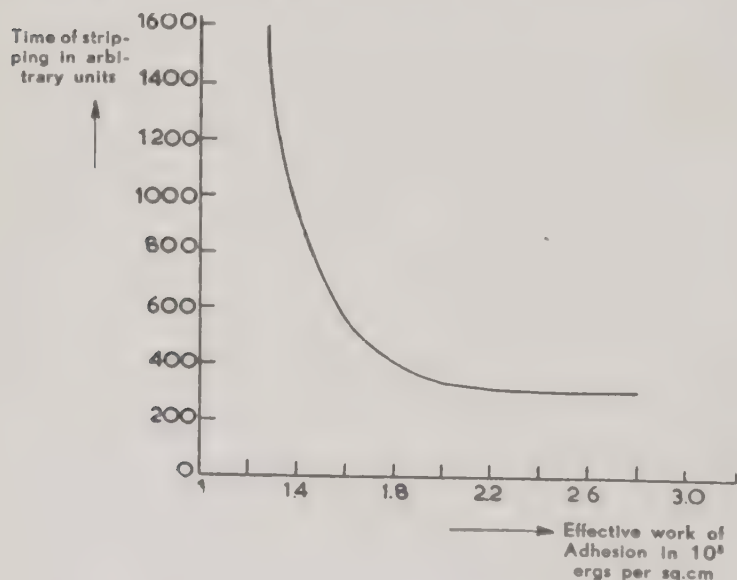


Fig. 22. Effective work of adhesion as a function of stripping time of surgery plasters.

References p. 28

is acting, is a very important factor. So is the thickness of the adhesive film, and in fact thin films of the same fluid show greater tackiness than thick ones. Keeping these facts in mind, we are able to understand the experimental results of R. S. RIVLIN³⁰, who measured the effective work of adhesion as a

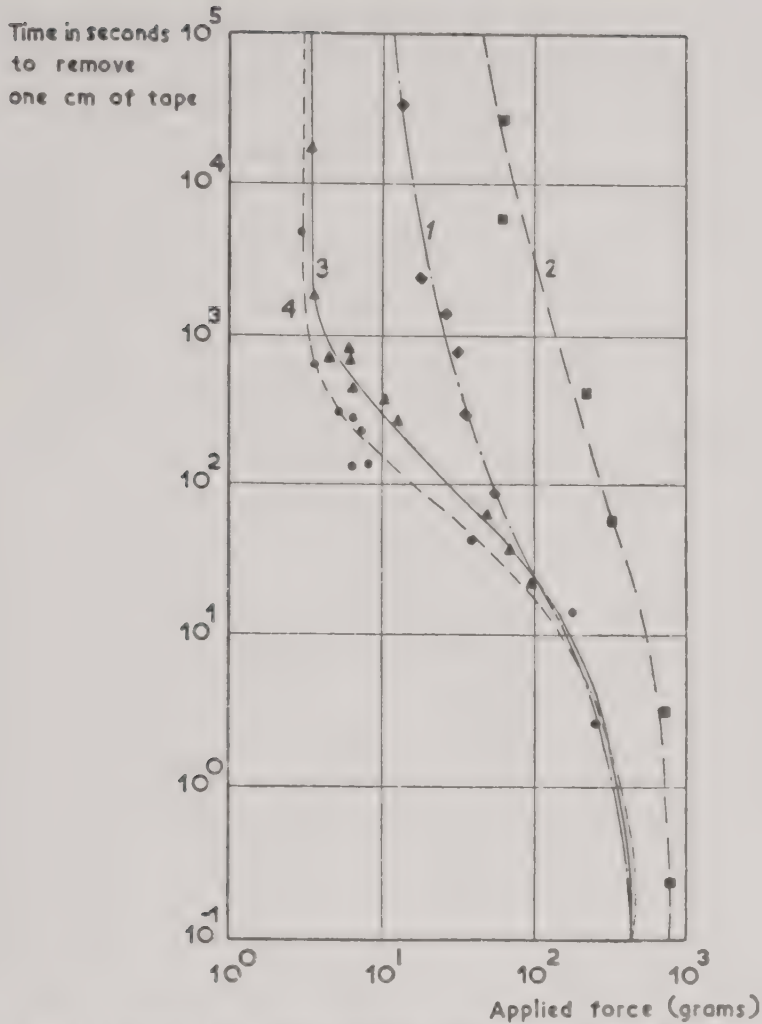


Fig. 23. Applied load plotted against rate of removal of pressure-sensitive adhesive tapes from a glass surface.
Curve 1 for natural rubber, Curve 2 for G.R.-S, Curves 3 and 4 for other synthetic elastomers.

function of the speed of detachment of an adhesive surgery plaster from a stainless steel plate. The chief constituents of the adhesive mixture, which was rolled on a substrate of woven fabric or a film material, were: masticated rubber, rosin, lanolin and zinc oxide. The effective work of adhesion varies with the speed at which the stripping of the tape is carried out, and this speed can be varied by taking other weights in stripping. So the effective work of adhesion can be plotted against the stripping time. A typical curve is shown in Fig. 22. These curves are very sensitive to the temperature at which the stripping is carried out. The curve in Fig. 22 shows that for relatively short times of stripping the effective work of

adhesion is very sensitive to variations of the stripping time. On the other hand, for relatively long times of stripping, the effective work of adhesion is not greatly dependent on the stripping time. The curve also shows that the measured values of the work of adhesion, varying between 10^5 and 3×10^5 ergs per cm^2 , are very high.

Other experimental results with adhesive tapes are reported by W. F. BUSSE, J. M. LAMBERT, R. B. VERDERY³¹, who measured the relation between

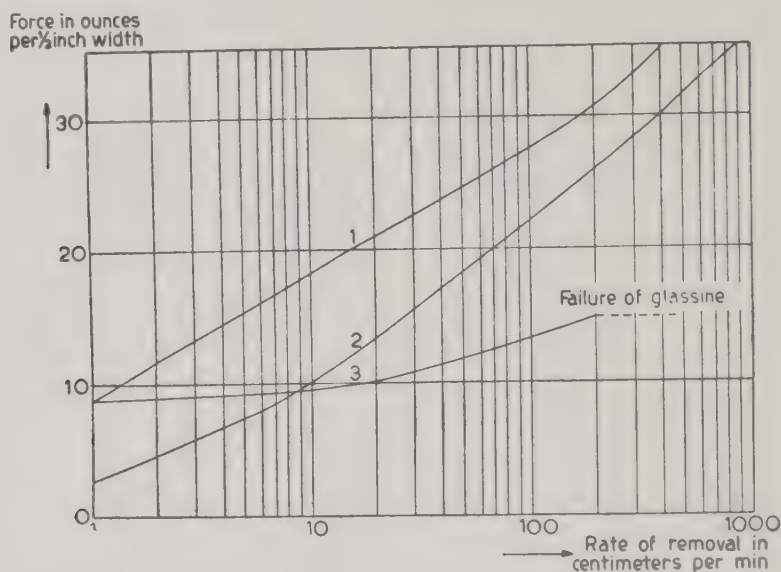


Fig. 24. Adhesion of "Scotch" brand transparent tape to (1) cellulose acetate, (2) cellophane, and (3) glassine, after one week of contact. Stripping angle 90° , temperature 25°C , relative humidity 50 %.

the applied load and the rate of removal of pressure-sensitive adhesive tapes from a glass surface at different temperatures. Typical results are given in Fig. 23. Curve No. 1 is for natural rubber, No. 2 for G.R.-S, Nos. 3 and 4 are for two other synthetic elastomers. The data illustrate the behaviour of the particular tapes rather than fundamental properties of the elastomers. The importance of the time factor in detaching tacky adhesives is also shown by Fig. 24, taken from the work of J. O. HENDRICKS, G. F. LINDNER and F. J. WEHMER³².

The curves give the adhesive force (in ounces per half inch width) plotted against the rate of removal (in centimetres per minute) for "Scotch" brand transparent adhesive tape on several adherent surfaces. Curve 1 shows the adhesion to cellulose acetate, 2 to cellophane and 3 to glassine after one week of contact.

These curves show that the rate of removal has a marked influence on the values of the separating force and that the change with rate of removal is different for different adherent surfaces. At low rates of removal, cellulose acetate and glassine are nearly equal. At higher rates of removal, the value on cellulose acetate increases rapidly, while the value on glassine increases but little. At low rates cellophane has a very low value, but it increases rapidly to quite a high value³³.

The question may arise whether an adhesive must be "long" or "short". In practice the "length" of an adhesive is estimated by taking some of it between index and thumb and drawing threads. If an "initial" tack is desired, a "short" adhesive must be taken. The plasticity diagram of such "short" substances shows a pronounced yield value at moderate shearing stresses and a low viscosity. If a join is established with such an adhesive having a yield value, deformation of the joint is immediately prevented by the adhesive layer. The "long" adhesives, without any yield value, but with a high viscosity, have the property of forming long threads. It is said that "long" adhesives have a higher adhesive strength than "short" ones. The yield value of "short" adhesives impedes excessive penetration into porous substances. This may be the cause of the higher adhesive strengths claimed for "long" adhesives, a moderate penetration being advantageous to obtain a strong joint. Secondly, high viscosity of "long" adhesives promotes adhesive strength.

The "stringiness" of adhesives, *i.e.*, the property of adhesives which permits of their being drawn out into long threads, may be due to a stretching or an orientation of long-chain molecules.

(d) *Theoretical Deductions respecting Tackiness*

The earliest work published on tackiness is that of J. STEFAN³⁴, who measured the forces necessary to separate two solid discs, immersed in a liquid, at a given rate. STEFAN used flat circular glass discs, immersed in various Newtonian liquids. The rate of separation was such that laminar flow of the fluid took place. The glass plates had an initial distance or separation h_1 and were pulled apart till the separation was h_2 , by a force F . With a viscosity η of the fluid used, the time t , required to separate the plates, is given by the equation:

$$t = \frac{3\pi\eta R^4}{4F} \left(\frac{1}{h_1^3} - \frac{1}{h_2^3} \right), \quad (1)$$

where R is the radius of the glass plates.

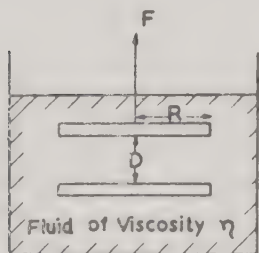
If $h_2 \gg h_1$, the expression $\left(\frac{1}{h_1^3} - \frac{1}{h_2^3} \right)$ may be replaced by

$\frac{1}{D^2}$, where $D = h_1$ is the initial distance of the plates.

In this case, equation (1) is transformed to:

$$t = \frac{3 \pi \eta R^4}{4 F D^2} \quad (2) \text{ See Fig. 25.}$$

O. REYNOLDS³⁵ made experiments, using two elliptical plates totally immersed in liquid, and arrived at equations which are fundamentally the same as STEFAN's.



$$t = \frac{3 \pi \eta R^4}{4 F D^2}$$

Fig. 25. Experiment and formula by J. STEFAN with Newtonian liquids between glass plates.

The mathematical derivation, which is rather difficult and elaborate in STEFAN's and REYNOLD's papers, is given with commendable clarity by J. J. BIKERMAN³⁶.

STEFAN's measurements were not in agreement with his theoretically derived equations. But if a correction is made of $d = 0,0015$ cm added to the D measured (initial separation), a far better agreement is obtained. The correction d must be added, as the effective initial separation was always slightly greater than the D measured, because of the roughness of the glass discs. J. Dow³⁷, taking this correction into account and recalculating STEFAN's data, showed that a linear relation is obtained between $4 F (D + d)^2$ and $3 \pi \eta R^4$.

The graph of these results is represented in Fig. 26, where $3 \pi \eta R^4$ is plotted against $4 \text{ gwt } (D + d)^2$; w being the applied weight in grams, so force $F = gw$.

STEFAN's equation may be written differently³⁸

$$Ft = \frac{3 \pi \eta R^4}{4 D^2}$$

The formula holds only for the first, but very important, stage of separating, where motion is so slow that laminar flow takes place in the adhesive.

The most probable next stage in separating the plates is a "necking down" of the fluid, forming one or more threads, which are ultimately broken. The other limitation in the application of STEFAN's equation is that the

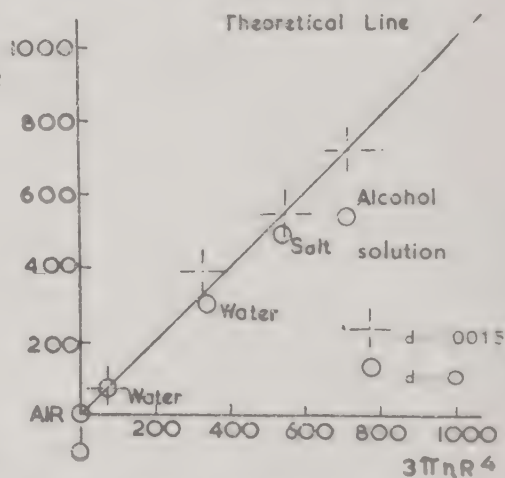


Fig. 26. Graph of J. STEFAN's results with correction by J. Dow.

liquid is Newtonian, which means that the viscosity of the liquid is assumed to be independent of the velocity gradient, which is produced in the fluid. In spite of these limitations, some very interesting deductions can be made from the above equation:

- (1) The force required to separate two solid plates between which there is a liquid layer is inversely proportional to the duration of its action. In other words separation requires an impulse Ft of a value given by the right-hand side of the equation. Thus the resistance to separation depends on the rate of separation and we cannot speak of one definite force opposing the breaking of the join.
- (2) The product Ft is directly proportional to the viscosity η of the liquid.
- (3) The product Ft is inversely proportional to the square of the thickness D of the fluid layer.
- (4) The "tackiness" of a Newtonian liquid is determined solely by its viscosity.

As F is inversely proportional to t , it is obvious that if t is very small, for instance when the joint is broken by a sudden pull, the force F may become greater than the tensile strength of the solids joined, and the adherends are ruptured and not the adhesive layer. This is shown in pulling off a freshly applied postage stamp from an envelope. A slow movement separates the adhesive, but a sudden movement tears the paper of either the stamp or the envelope. The "picking" or "plucking" of the paper by too tacky a printing-ink at high-speed pressing is another example.

If the viscosity η of the fluid is very high, for instance if we are dealing with natural asphalts, and if we take a very thin layer, the value of Ft becomes very large. A numerical example is given by J. J. BIKERMAN³⁹.

If we take $\eta = 10^8 \text{ g cm}^{-1} \text{ sec}^{-1}$ and $\frac{1}{2} \pi R^4 = 10 \text{ cm}^4$, an Ft value of $\frac{10^9}{D^2}$ results.

This means that an asphalt layer of 10^{-4} cm thick between two discs of 1.4 cm radius should resist a pull of 10^{17} dynes for 1 second, and that of 10^{10} dynes (corresponding to about 1600 kg/cm^2) for nearly 3 months. Actually the asphalt layer will break immediately under a much smaller load. It will rupture, not flow to any measurable extent, and for its rupture not STEFAN's equations, but the laws of strength of material will hold. In this case rupture will begin in a weak spot, along one or more flaws, which are always present in such materials as asphalt. A microscopic flaw will grow very fast to a real ruptured surface.

In STEFAN's formula the plates are assumed to be totally immersed in

the liquid. However, if we have a drop of Newtonian liquid of a volume V between two parallel plates and measure the time necessary to separate them, we get the expression:

$$t = \frac{3 \eta V^2}{8 \pi F D^4} \quad (\text{See Fig. 27}).$$

Here η is the viscosity of the liquid, V the volume of the liquid, F the pulling force, D the initial separation of the plates. This formula is derived from a formula given by HEALEY⁴⁰ who gave the time t necessary to compress a drop of Newtonian fluid from an initial separation h_2 to a separation h_1 of the plan parallel plates. In the above formula it is assumed that the liquid initially fills the whole space between the two plates, so $V = \pi R^2 D$ if R is the radius of the plates.

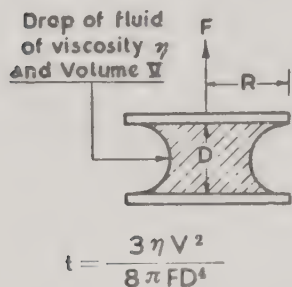


Fig. 27. HEALEY's experiment and formula. Drop of fluid of viscosity η and volume V between flat plates.

If we compare HEALEY's equation with STEFAN's, it appears that the times differ only by a factor $\frac{1}{2}$, that is: $t_{\text{HEALEY}} = \frac{1}{2} t_{\text{STEFAN}}$.

If we have a drop of non-Newtonian fluid between two parallel plates, account must be taken of the variation of viscosity with the rate of shear. If the rate of shear dv/dy of the liquid is related to the shear stress τ by an equation of the form $\frac{d\tau}{dy} = \Psi(\tau - f)^n$, where f is the yield value and Ψ is the mobility of the fluid⁴¹, we may employ the analysis of J. R. SCOTT⁴², and come to the following expression for adhesives with a yield point (*i.e.*, f is finite) and a value of $n = 1$:

$$F_L = \frac{2fV^{\frac{3}{2}}}{3\pi^{\frac{1}{2}}D^{\frac{5}{2}}}$$

F_L is the limiting force, beyond which no separation will take place, V is the volume of the drop, D the thickness of the adhesive layer.

In all of the above considerations, surface tension is neglected. Surface tension effects become appreciable with thin layers of adhesive. If both plates are wetted by the adhesive, there will be a force of attraction acting normally to the surfaces, given by the equation:

$$F_T = \frac{2VT}{D^2},$$

where V is the volume of the drop, T the surface tension between liquid

and air, and D the distance between the plates.⁴³ It follows from this equation that, unless the applied load is greater than F_T , no separation will take place, though sliding motion may occur (which in practice is even more objectionable). F_T is inversely proportional to the square of the thickness of the layer and decreases rapidly with increasing D . From the above considerations it follows also that resistance to motion due to surface tension forces is not only a function of the properties of the adhesive, but also of the nature of the adherend surfaces, since these too will determine the angle of contact between adhesive and adherend surfaces.¹

In the above considerations we assumed that the motion of separation is slow enough for laminar flow to occur in the adhesive. If a strong separating force is applied abruptly, the film breaks down without laminar flow, leaving a characteristic tree-like pattern on the surface of the adherend as is shown in Fig. 21⁴⁴.

In practice we have more complicated conditions than those supposed in the above theoretical considerations. For instance, the rheological properties of the adhesive may be highly complex, they may vary continuously with time, due to evaporation, gelatination or setting. However, we may draw some general conclusions and may give some requirements for obtaining a high degree of tackiness and a high adhesive strength with adhesives.

The desiderata are:

- (1) The thinnest possible spread. In all the above equations the resisting force increases with decreasing thickness of adhesive.
- (2) An adhesive with a yield point.
- (3) An adhesive of high viscosity.

The third requirement conflicts with (1), but this may possibly be overcome by using a thixotropic adhesive, by hot application or by application in solution (see sub-section (a), p. 46).

(e) *Measurement of Tackiness in Practice*

As the definition of tack is very obscure, obviously it is very difficult to propose methods for measuring it. Each special branch of industry attaches its own meaning to tack and makes its own demands upon it. The best course in each particular case is, therefore, to correlate the required tackiness with a physically measurable property of the adhesive material.

The earliest measurements of tack were those made by STEFAN (*loc. cit.*³⁴) and REYNOLDS (*loc. cit.*³⁵). (See sub-section (d), p. 63-64). They investigated Newtonian liquids between flat plates, which had a circular or

elliptical form. They measured the rate of separation of the plates when known separating forces were applied. One of the first to try to measure the tack of printing-inks was J. BECK⁴⁵. He measured the movement of a hemisphere located in a recessed plate when the hemisphere was covered with a thin layer of printing-ink and various forces were applied to it. BECK stated that a relationship exists between tack and viscosity, but made no attempts to find the mathematical relationship. Experimentally he found the important fact that very thin ink layers of the order of 5 to 10 microns behave differently from thicker ones, and also that they rupture rather than „neck down” under a separating force. R. F. REED⁴⁶ devised an instrument, called the “Inkometer”, composed of two rotating cylinders that are inked and in mutual contact. The ink causes a resistance to the rotation of the cylinders, which acts as a torque. This torque is recorded by a lever device and is defined as “tack”. Essentially, the Inkometer indicates the shearing forces in the ink layer between the rollers at their contact area. The results cannot be given in independent units, but must be given in terms dependent on the instrument. The Inkometer has been successful in the prediction of ink “trapping” in multicolour printing, where successive films of inks can only be satisfactorily printed one upon another if each following ink has less tackiness than the preceding one. The Inkometer has the advantage of enabling different inks to be compared with it at different press speeds.

A very old, subjective, method of measuring tack is the so-called “finger tab-out” test, by which the finger is pressed upon a thin film of the tacky material and then withdrawn suddenly. An attempt to construct an apparatus imitating this finger-tab method by means of a mechanical “finger tip” and a quantitative evaluation of the forces involved, has been made by H. GREEN²⁶. His instrument is called “the Tackmeter”. The tackmeter measures the pull resistance of ink layers and shows the relation of tack and relative tack to yield value and viscosity. This relationship can be determined by an apparatus that splits or partially splits the film, as the tackmeter does. GREEN gives a relationship between the coefficient of viscosity μ , the splitting force and the splitting time t as follows:

for liquids:

$$\mu = \frac{(D + d)^2 w \cdot 4.6 \cdot 980 t}{\pi R^4}$$

and for plastic materials:

$$\mu = \frac{(D + d)^2 (w - k) \cdot 4.6 \cdot 980 t}{\pi R^4}$$

D is the initial thickness of the liquid or plastic layer; d is a constant correction factor; w is the weight placed on the lever of the instrument, 4.6 the

lever factor of the instrument, 980 the acceleration. So the actual force F equals $w \cdot 4.6 \cdot 980$; R is the radius of the area of contact, k is the yield value. GREEN comes to the conclusion that the "relative tack" of a printing ink, i.e. the tack of the ink, divided by that of a standard substance such as a stable mineral oil, is a useful property. At high speeds, high rate of break, the relative tack depends almost entirely on the viscosity. For high rates of break the relative tack is reduced to a ratio of the plastic viscosity of the ink under test and that of the standard material.

An apparatus, constructed and described by A. VOET⁴⁷, somewhat similar to that described by B. W. DERJAGIN and A. P. PORITSKAJA⁴⁷,

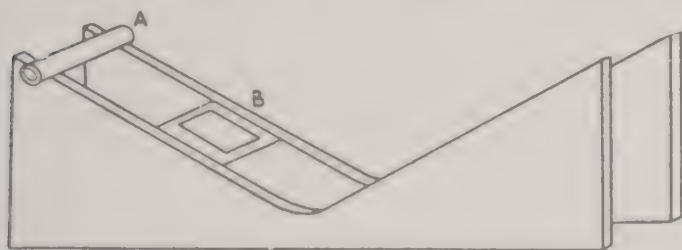


Fig. 28. Apparatus constructed by A. VOET to measure the tack of printing inks.

takes due account of the fact that in the practice of printing the ink is generally printed on paper. The influence of the paper is discussed in a previous publication by the same author⁴⁸. VOET's apparatus (See Fig. 28)

consists fundamentally of a cylinder A which, upon being magnetically released, moves down a plane, formed by two U-shaped bars, and rises again on the second plane as a result of the momentum obtained. The greatest height reached is now recorded. In a companion test the experiment is repeated, but a small inked plate B is placed in the path of the cylinder, causing adhesion of the ink to the cylinder and thus film splitting. The difference in height attained by the cylinder in both tests indicates the energy needed for the ink film splitting. The cylinder may be covered with papers of different characteristics. The speed as well as the weight of the cylinder may be varied, in order to imitate different conditions on a press. It is possible to measure tack on this instrument in fundamental units, in a thin film, at a definite speed and at a known pressure, the separating surfaces being paper and metal.

As we have seen that the conception of tack is not the same in different industries and there is a lack of agreement on its definition, it is unlikely that any one method of measuring tack will find general application. It is obvious that the best tests consist of a method approximating as nearly as possible the conditions under which the adhesive is used in practice. Adhesive tape, for instance, is tested by means of pulling it away from a surface at a known rate of loading, during which the pulling force is

measured. R. S. RIVLIN³⁰ uses a vertically placed polished stainless steel plate, on which is rolled a length of adhesive tape. A weight is attached to the upper end of the tape and the tape peeled off slowly. By taking other weights, the time of stripping may be varied. In doing so, RIVLIN measures the stripping time as a function of the effective work of adhesion and by plotting the data gets curves like that of Fig. 22.

A similar very simple device for the testing of adhesive tape described in British Standard 1133, is illustrated in Fig. 29. The double-back tape,

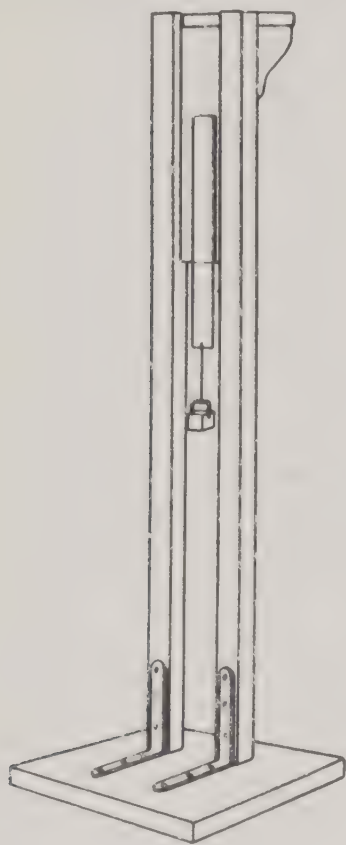


Fig. 29. Peeling test according to B.S. 1133.

which is stuck to a vertical surface, is peeled off by a load of three ounces per inch of width. The temperature is kept constant at 60° F during the tests. The tape should not strip at a rate exceeding one inch per five minutes to satisfy the requirements of the test.⁴⁹

Two devices to measure tack in the rubber industry are described by W. F. BUSSE, J. M. LAMBERT and R. B. VERDERY³¹. The first apparatus measures the applied load at different rates of removal of pressure-sensitive adhesive tapes from glass surfaces. For the results see Fig. 23, p. 61. The apparatus consists of a glass plate, fastened to the pan of a direct reading scale. The adhesive tape is fastened to the top of the glass plate and the free end of the tape is pulled perpendicularly to the surface by means of a cord which passes over a roller and another pulley driven at the desired speed.

The second apparatus described in the same paper is a tackiness-tester for rubber mixtures. It measures the resistance to separation of sheets of rubber under various conditions. One strip of rubber is fastened to the pan of a pre-loaded spring scale, which reads compression and tension loads directly. Another sample of the rubber is put around a mandrel, 3.4 cm in diameter and 2.5 cm wide, and lowered by a motor and drive in a 2.4 sec. cycle. The rubber samples are pressed against each other with a force of 565 g at the bottom of the stroke and then pulled apart. The maximum position of the scale pointer on the return stroke of the drive

is read. This value, when corrected for the inertia effects of the system, is a measure of the force required to separate the samples, *i.e.* of the tackiness of the rubber mixture.

In a recent patent on the manufacture of adhesive compounds⁵⁰, numerical values are given for the rheological or flow properties of silicate-clay adhesives for use in the manufacture of corrugated fibre-board. By adding a specially prepared clay suspension to a sodium silicate solution it is possible to obtain an adhesive mixture having a yield point of 25 to 150 dynes per sq. cm, a mobility coefficient of 0.3 to 0.4 rhés * (preferably 0.4 to 0.6), and a "thixotropic ratio" greater than about 1.3. These values are equal or approach to the ideal values required for use on a corrugated or solid fibre-board machine. The following definition is given of the thixotropic ratio: The apparent average viscosity is determined by using a calibrated Stormer viscometer, at 10 and at 100 revolutions. The former viscosity divided by the latter gives the thixotropic ratio. The ratio is 1 for a non-thixotropic material; for a thixotropic material it is greater than 1, and the difference from 1 is a quantitative measure of the thixotropy of the adhesive. This thixotropic ratio is a purely empirical expression for the degree of thixotropy associated with a system, but it proves valuable in comparing silicate clays.

(f) *Setting of the Adhesive*

The adhesive can be caused to set by cooling to room temperature, by (further) drying out, or by chemical action. Cooling may result in considerably increased viscosity, in the occurrence of a yield value or even in the crystallization of the adhesive or of part of the adhesive.

Solutions of adhesives and also molten adhesives show very pronounced temperature coefficients of viscosity.

The occurrence of a yield value has been mentioned earlier in relation to protein glues.

In cooling molten plastics of the polymer (one dimensional type), crystallization will often set in and cause a yield value. Because of the great length of most polymer molecules, crystallization will only bundle the parts of long molecules that happened to be lying side by side in the fluid mass. The crystallization of these polymers thus gives rise to crystallites of restricted dimensions, with fringes of entwined molecules at both ends. These crystallites have been proved to exist both in natural and in several synthetic rubbers, and are very marked in polyethylenes. The rubbers

* The rhe is the inverse of the poise.

themselves are not fusible, but are often used as additives to molten masses (*e.g.* mixes of rubbers and resins, well-known adhesives for rubber flooring, for pressure-sensitive tape, etc.). The crystallites mentioned play the same rôle as the bonds formed by sulphur in the vulcanization of rubber: they form the knots in a network of long threadlike molecules.

The drying out is the same process that was discussed when speaking of the application of dissolved adhesives; for such dissolved adhesives the process of application and of conversion into the solid state may be seen as one stage. Somewhere during this conversion, the half-dried adhesive passes through the state of tackiness; at this point the parts are joined. It has already been stated that the remaining solvent has to be able to diffuse through the adherends. It is clear that this class of adhesives, which sets by drying out, is unsuitable for joining metal parts.

Chemical action, converting applied adhesives from the liquid to the solid state, is the modern way of hardening synthetic adhesives. The adhesive mostly consists of two chemical compounds, able to interact under the influence of heat, catalysts or both. The chemistry of these processes must be left to the specialized parts of this book. The rheological consequences are to be seen as an increase of viscosity, followed by the building up of a yield value.

Of chief concern to us is the fact that most of these chemical solidifying reactions involve a change in volume, mostly contraction. Inasmuch as this contraction happens during the highly viscous or the plastic stage of the adhesive, nothing will occur but a slight decrease in thickness of the layer. However, if big gaps exist between the adherends, holes may appear in the bulk of the adhesive filling the gaps. But the contraction mostly goes on when the adhesive has already been converted to a solid or even a brittle state. In this case, cracks may occur in the adhesive layer on hardening, reducing the strength of the joint to almost nothing. This phenomenon is very serious when big holes between the adherends have to be filled with the adhesives. The so-called "gap-filling" adhesives have been developed for just these cases. They show little contraction on hardening, and mostly contain plasticizers so that the yield point of the hardened glue shall be below the breaking strength. By this means the stresses originating from the chemical contraction can be neutralized by slight interior flow.

The cracking and contraction of adhesives is in practice a very serious drawback to several simple glues of the three-dimensionally condensing type. Linear polymers are much less dangerous in this respect, for most linear polymers are less brittle than three-dimensional ones.

§ 3. RHEOLOGY OF HARDENED ADHESIVE LAYERS

In this third part of our chapter on the rheology of adhesives we propose to discuss the finished joint. We shall consider the rheological aspect of five different properties of the set adhesive largely determining the behaviour of the joint under different circumstances, *viz.*:

- (a) Plastic flow of the adhesive.
- (b) The elastic modulus, as compared to that of the adherends.
- (c) Expansion and movements of the adhesive layers through adsorption of fluid (water).
- (d) Building-up of inner stresses in the adhesive.
- (e) Influence of temperature on these properties.

But before entering upon this discussion, we must first deal with some general properties of a joint. Once a joint has been formed and the adhesive has solidified, properties of the adhesive other than those mentioned in Section 2 come to the forefront. One factor is the tensile strength of the adhesive, which, as we shall see, is not the same as that of the joint made with it.

A film or layer of adhesive in a joint shows a greater strength both in tension and in shear than the same adhesive material in bulk. This has been confirmed by many experiments. In this regard the work of MCBAIN and co-workers⁵¹ heads the list of investigators. In addition to the above-mentioned effect, *viz.* that the joint strength of adhesives is greater than the bulk strength, MCBAIN found another effect during his experiments, i.e., increasing joint strength with decreasing thickness of the adhesive layer. MCBAIN formulated this effect as follows: "The thinner the adhesive layer, the stronger the joint. The effect of thickness is not appreciable with thick films, but rapidly increases when the thinnest possible films are studied". The results of MCBAIN's experiments with shellac adhesives on nickel and aluminium are illustrated by Fig. 48 in Chapter 4 of this book by C. MYLONAS and N. A. DE BRUYNE. The experimental facts of an increasing joint strength with a decreasing thickness of the adhesive layer are in full agreement with the theoretical deductions about tackiness (See § 2 p. 63-67). If we consider STEFAN's formula for the separating force of two plates between which is a liquid (adhesive) layer, we may deduce from it that the separating force F is inversely proportional to D^2 , the square of the thickness of the liquid layer. From the same pages we see that the HEALEY formula for a drop of liquid between parallel plates even shows a separating force F falling off with $\frac{1}{D^4}$ where D again is the thickness of the liquid layer,

and finally the separating force for an adhesive with a yield point between parallel plates shows inverse proportionality to $D^{\frac{5}{2}}$.

Extremely thin layers of liquids were investigated by H. M. BUDGETT⁵², who used optically polished steel surfaces true to one millionth of an inch, which he brought into very close contact by wringing. The adherence of the metal surfaces was dependent upon the presence of an extremely thin liquid film. BUDGETT was able to show that in his experiments the thickness of the film was of the order of a few millionths of an inch, that is of the order of a few hundred molecules.

With condensed water vapour or oils between the plates, the tensile strength of the joined surfaces was rather high, whereas the clean dry surfaces could be separated by a small force. BUDGETT concluded that his liquid films were very incomplete and that not more than 4% of the force required to separate the surfaces could be ascribed to the surface tension of the liquids. The effect was essentially due to the cohesion of the liquid; the rupture always occurred in the liquid itself and not at the solid-liquid interfaces. Even in these experiments, where the thickness of the films is extremely low, the breaking load very rapidly increases as the film gets yet thinner. The adhesion of these precision-finished steel blocks has been the subject of much theoretical discussion with respect to the polar attraction of molecules. An accuracy or smoothness of the blocks of 10^{-6} inch may be achieved by special measures⁵³.

The importance of thin surface films in promoting adhesion between gauge blocks is also emphasized by F. D. JONES⁵⁴. JONES states that, when the blocks are perfectly clean, they fall apart by their own weight, but with oils and water vapour, especially with water vapour and a trace of soap, the separating forces are considerable. See also Chapter 4 by C. MYLONAS and N. A. DE BRUYNE. In agreement with the results obtained by MCBAIN and LEE, many other investigators found an increasing joint strength as the thickness of the adhesive was diminished. J. J. BIKERMAN⁵⁵ checked the experimental results of MCBAIN and LEE with paraffin wax joints between metal surfaces. His experimental results were exactly the same as those of MCBAIN and LEE, *i.e.* for thin joints ($57\ \mu$) an average joint strength of $24.6\ \text{kg/cm}^2$ was found and for the thick joints ($540\ \mu$) $14.8\ \text{kg/cm}^2$. W. P. KONSTANTINOVA⁵⁶ found tensile strengths of the same order as MCBAIN and BIKERMAN with paraffin wax joints thinner than $0.01\ \text{cm}$, and a tensile strength of $7.45\ \text{kg/cm}^2$ for the wax in bulk. With decreasing thickness of layer, an increase in strength of joint was found of the same order as that reported by BIKERMAN and MCBAIN.

In the gluing of wood, several investigators emphasize that the glue film must be very thin for strong joints. J. W. MAXWELL⁵⁷ investigated

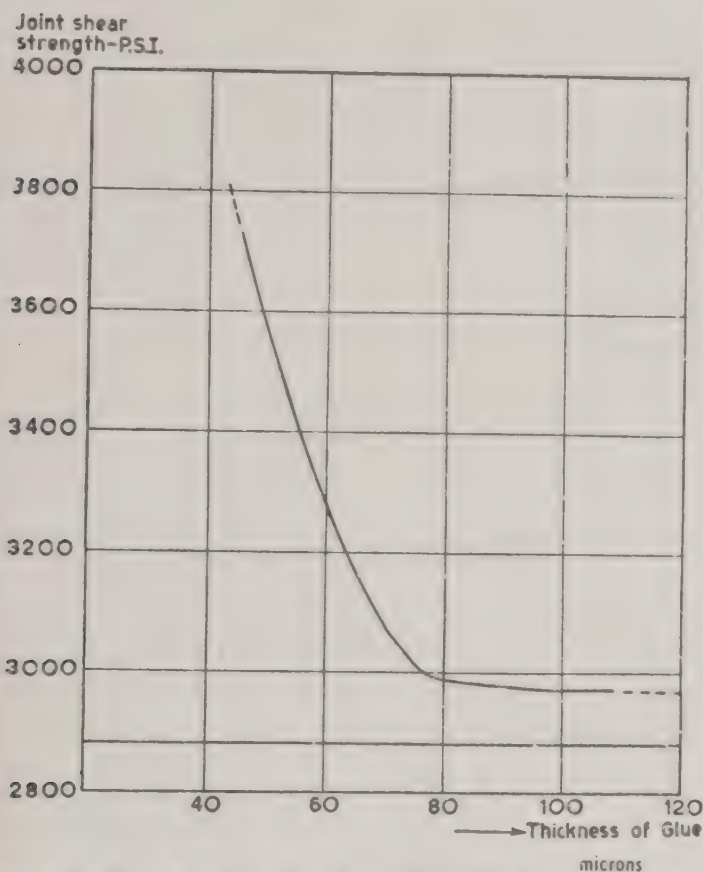


Fig. 30. Joint shear strength of resin glue in relation to thickness of glue film.

J. W. MAXWELL, *Trans. Am. Soc. Mech. Engrs*, 67 (1945).

the shear strength of wood joints with resinous glue as influenced by the nature of the wood surface and the pressure on the joint during the gluing operation. He also investigated the influence of the thickness of the glue film. His results with planed, *i.e.* relatively smooth-surfaces, are shown by the curve in Fig. 30. This Figure shows that the joint strength, which is rather high for very thin glue layers, diminishes rapidly to a point where the glue film thickness approaches 80 microns. Beyond this

film thickness the joint strength remains relatively stable. The shear strength of the glue in bulk was 2800 P.S.I. So the joint strength may be 200–1000 lbs. stronger than the glue strength, as can be seen from the Figure. In Fig. 31 the results of POLETIKA's investigations⁵⁸ with plywood joints are shown, giving approximately inverse proportionality between joint strength and glue line thickness. The strength of soldered metal joints, investigated by T. B. CROW⁵⁹, shows a similar tendency with respect to the thickness of the solder. The tensile strength of the joints increases with decreasing thickness of the solder film. The strongest soldered joint investigated had a tensile strength of some 2.5 times that of the solder. In the case of soldering metals, the influence of partial diffusion of the metals and the solder into each other and alloying at the contact surfaces should be considered.

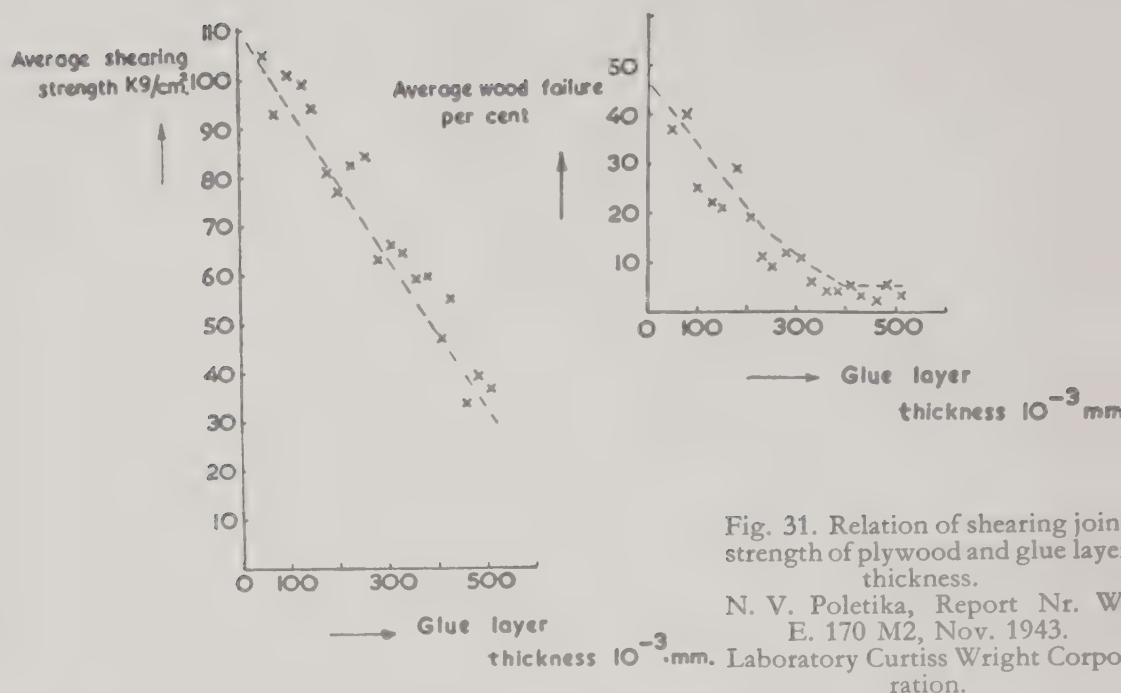


Fig. 31. Relation of shearing joint strength of plywood and glue layer thickness.

N. V. Poletika, Report Nr. W E. 170 M2, Nov. 1943. Laboratory Curtiss Wright Corporation.

Explanation of the results with thin adhesive layers.

McBAIN and LEE⁶⁰ tried to account for the results found in their experiments. They suggested that the higher strength of thinner joints was due to long-range molecular forces operating between the metals and the interior of the adhesive film. In their reasoning, not only the molecules of the adhesive which actually touch the surface are orientated, but "whole chains of orientated molecules extend from the surface of the adherend well into the liquid or solidified adhesive". Later investigations, *e.g.* those of R. BULKLEY⁶¹, revealed, however, that attractive forces between surfaces and adsorbed layers do not operate through much more than a monomolecular layer of a liquid.

In complete agreement with these views of BULKLEY's are the calculations of the electrostatic attraction between surfaces and charged particles by J. E. LENNARD JONES⁶², and the work of F. P. BOWDEN³³ on the range of surface forces.

J. J. BIKERMAN⁶⁴ has another theory to explain the decrease in tensile strength if the thickness of the adhesive is increased. He does not believe in long-range molecular forces, but he analyzes his own experimental data on paraffin wax joints by a simple application of probability. With his "probability of flaws" BIKERMAN explains $\frac{2}{3}$ of the differences between thick and thin wax joints. The remaining third he ascribes to crystallization differences between thick and thin sections of paraffin wax

between metal blocks. BIKERMAN's reasoning is as follows: the tensile strength of a rod or a fibre depends on the length of the specimen: the shorter the fibre, the greater the strength. For a long rod or fibre is likely to show more faults or flaws than a short one. These faults or flaws cause the rupture of solids under stress. The rupture will occur at the weakest spot. This theory of flaws, which was checked and proved to be satisfactory for fibrous materials, can be applied to glued joints as well. When the length of the "rod" is gradually reduced, the rod becomes a plate and then a film. In reducing the length of the rod, the tensile strength increases, for if the rod is uniform, the probability of finding a weak spot decreases with the length of the specimen, *i.e.* the thickness of the glue layer. The rule: "the shorter the fibre, the greater the strength" is confirmed by experiments with several fibrous materials, *e.g.* with cotton hairs by F. T. PEIRCE and K. C. BROWN ⁶⁵, with rayon threads by H. R. BELLINSON ⁶⁶, and with glass fibres by F. O. ANDEREGG ⁶⁷.

The mathematical relations between the frequency curves of strength and the length of the specimen are discussed in full detail by F. T. PEIRCE ⁶⁸, and his calculations are in good agreement with the experimental data.

Preliminary Conclusions as to Joint Strength

The literature survey given here, which is by no means exhaustive, shows that a lot of work has been done on this problem. As a result, it is now certain that thinner joints are stronger, that part of the influence can be ascribed to the greater probability of flaws in thick joints, and that far-reaching orientation in adhesives is not acceptable because of modern views on the range of surface forces. But notwithstanding all the work done, the present authors hold the view that the problem has not been studied from all angles. In the first place, the many adhesives and solders which exhibit plastic flow before they break will be hindered from doing so in thin layers. M. ZSCHOKKE and R. MONTANDON ⁶⁹ have interpreted the influence of the thickness of solder layers on their strength as an example of restraint of deformation. It may be understood in the following way. If a piece of material which can be plastically deformed is strained, *e.g.*, if a cylindrical test piece is drawn out, its cross-section begins to decrease, usually at the weakest point *. The cross-section, which eventually breaks,

* This is not true for materials like steel and copper, which stiffen on deformation; such materials mostly decrease in cross-section over the whole length of the test piece before any failure occurs. The organic materials nowadays used as adhesives include several high molecular weight polymers showing this stiffening effect. The effect is caused here by orientation and orientated crystallization. Such materials, when used as adhesives in thick layers, will therefore possess a certain advantage over materials that do not stiffen upon deformation.

is much smaller than the original one. A layer of solder or adhesive may be considered as a very short bar with a very large cross-section. But the decrease in cross-section found in the strained test bar is now greatly held in check, as the material tested lies sandwiched between the flat adherends.

For the movement of such a layer between flat surfaces compare the theory of parallel plate plastometer ⁷⁰.

If we have to do with a very thin layer, flow will be almost impossible and the ultimate fracture will take place in a cross-section equal to the original one. Therefore, the solder or plastic adhesive, when tested in a thin layer in a joint, will show far greater breaking strength than when tested as a bar. This is due to strong restraint of deformation.

So the literature gives us two reasons why thin layers of adhesive provide stronger joints, *viz.*, (1) fewer flaws in thin joints; (2) restraint of deformation.

A third reason for the extra strength of thin joints

There is a third and very important reason why joints with thin glue layers will be stronger than those with thick ones. The authors have not found any reference to this reason in the literature, but they think it to be of the first importance in all cases where the adhesive layer is of a rigid, non-yielding character. When a glued joint fails, this is often due, not so much to forces at right angles to the surface, as to stresses parallel to it. Tangential stresses in adhesive coats are often very strong for various reasons, including shrinkage of the adhesive, swelling of the adhesive, difference in thermal expansion between adhesive and adherend, etc.

We shall revert to these matters in the following paragraphs. When an adhesive is torn from its adherend, this is mostly caused by a combination of tangential and perpendicular forces. The former originate in internal stresses, the latter from external forces. When considering thin layers, however, one may say that these internal stresses will always be proportional to the thickness of the glue layer. It will help us to understand this if we suppose that such a layer will tend to contract, owing to, say, the loss of included solvents, or chemical reactions, or cooling from a higher to a lower temperature. If this contraction is impeded, the contracting internal stresses will be limited by the yield value of the material; but up to this point the contracting forces will always be proportional to the thickness of the layer. This proportionality is clear if we consider the adhesive layer as built up of several very thin layers. Each of these, taken apart, sets up contracting forces. The contracting forces of the total layer are the sum of all the forces of the thinner layers into which the whole layer is subdivided.

Restraint is exerted in the case of adhesive layers between adherends by

the adhesion to the surfaces. The tangential forces set up in this way on the borderline between adhesive and adherend are caused by the said contracting forces and thus they are proportional to the thickness of the glue layer. The adhering forces have to counteract the sum total of the contracting (or expanding) forces set up by the whole body of the glue layer. This simple reason may very well be the main reason why thin adhesive layers should generally be preferred. A thin layer of adhesive may shrink or expand or swell just as much as a thick one, but the forces exerted by the thin one in such a case will be less than those exerted by the thick one. Therefore the adhesion will be endangered much more by such swelling or shrinking of a thick layer than of a thin one.

Now that we have discussed joint strength and joint thickness at great length, we propose to give our attention to the four different properties of adhesives mentioned at the beginning of this § 3, as, each in its own way, they influence the behaviour of a joint rheologically.

(a) *Plastic Flow of an Adhesive*

When an adhesive has a very low yield value, but high viscosity, it is a very suitable adhesive for supple, deformable adherends. Deformability of the adhesive is very high, but plastic adhesives are never suitable for rigid joints. It is evident that with such an adhesive no joints of anything like high or even moderate breaking strength can be realized; shocks and stresses of short duration may well be resisted, but in due course any continuous loading will give rise to permanent deformations. The adherends will begin to glide very slowly over each other when under permanent shearing stress; and when they are under a permanent pull at right angles to the adhesive layer, they will separate in the long run, if this pull exceeds the yield value*.

Moreover, as explained in § 1, the yield value of these permanently plastic adhesives is often merely fictitious; at stresses under this value a very slow but steady deformation or creep sets in. Plastic adhesives, however, possess one very great advantage over all the others, the highly elastic ones excepted. This advantage is commonly regarded as being firm adhesion, but this adhesion is only apparent. The valued effect is produced, not by interfacial energies (see Chapter 1 on Adherence), but by the rheological properties of these adhesives. As has been shown in the general introduction of this § 3, a joint is endangered in the majority of cases by tangential stresses on the borderline between adhesive and adherend. These stresses may over-

* See, however, page 66-67 on the effect of surface tension (on tackiness).

come the adhesion, possibly together with a pull in a perpendicular direction or, if adhesion does not fail, these stresses may cause fracture within the layer of glue. The latter will occur if the cohesion is weaker than the adhesion. This rule, however, only holds if the material shows a yield value which is decidedly higher than the stresses originating in the borderline. Now this is certainly not the case with plastic adhesives; with them, all tangential stresses originating in the borderline will disappear directly there is any internal movement or relaxation. For this reason, plastic or highly viscous materials exhibit great (apparent) adhesion. The unreliability of a permanently loaded joint and the apparent strength of adhesion (i.e. the fact that adhesion is maintained) are due to the same cause. Some bituminous adhesives, or those consisting of mixtures of bitumen and resin, however, will break away from the surface completely when the whole assembly is subjected to sudden heavy stress, so short as to allow no time for relaxation or internal movements: the adhesion fails under impact. The reason for this is that such abrupt loading of the joint allows no time for the initiation of the very slight flow which usually neutralizes all stresses set up in these plastic adhesives. Plastic adhesives that fail under this impact test are nevertheless an exception. The tangential or parallel stresses mentioned in this chapter are the supreme enemy of all "strong" glues, but with these creeping glues they are non-existent. In them all inner stresses are neutralized by the internal viscous flow.

Plastic adhesives can only be used within a very limited range of temperatures; when cooled down to well below room temperature they have a tendency to become brittle. Above room temperature their yield value will decrease further and their viscosity will fall exponentially; they will lose all their strength. As examples of plastic adhesives we may mention asphaltic bitumen, pressure-sensitive tapes (consisting, *e.g.*, of rubber, resin and plasticizer), polyvinyl acetates of low molecular weight ("Gelva", "Vinnapas"), cyclized rubber ("Vulcabond", "Bostik"). Such adhesives will paste anything together, but the bond does not last under even moderate stresses if these stresses are permanent.

(b) *Elastic Modulus, as compared with that of the Adherends*

The elastic modulus plays a very important part in adhesives. To begin with, we shall have to consider the class of highly elastic adhesives, showing very low elastic moduli.

Rubber solutions, highly elastic plastics, latices, find widespread use for joining rubber-like and pliant adherends. These materials do not possess

great breaking strength, whereas their deformability is very considerable; but they generally have a marked yield value. Joints made with them are therefore stable under prolonged pulls and stresses below certain limits. Because of their low elastic moduli, stresses on the borderline will not be built up to any appreciable extent, since in this case substantial expansion or contraction of the glue layer or adherends will not produce great stresses in the adhesive. These highly elastic adhesives are therefore more useful than the plastics. Since, however, a chain is as weak as its weakest link, adhesion must be better here than the real adhesion of the permanently plastic ones. As examples we name rubber solutions and latices of india-rubber and synthetic rubbers.

Passing on to materials of higher elastic modulus, we find that it will be prejudicial to the conditions in a joint if the elastic modulus of the adhesive exceeds that of the adherend ⁷¹. For, what will happen if a joint containing an adhesive of high elastic modulus is deformed? Let us imagine the adhesive sandwiched between "soft" adherends. If the whole is strained by simple shear, the adherends will be deformed to a greater extent than the adhesive. If the adherends are stretched, the adhesive will be stretched to less extent by the same deforming force. The consequence will be very great tangential or parallel shearing stress at the boundary. Where we have two strips of a certain elasticity, joined by a harder glue line, we shall find that the strength of the joint has much decreased, because a preponderant proportion of an applied tearing force will act on the extreme left and right ends of the boundary between adhesive and adherend only. Corresponding stresses are set up in the adjoining adhesive layer and, if the adherend does not fail locally, the adhesive will do so. See in Fig. 36 Chapter 4 by C. MYLONAS and N. A. DE BRUYNE in this book the point between the left extremity of the glue line and the upper strip and between the right end of the glue and the lower strip. See the same Chapter for an explanation of these stresses. The inference is that the elasticity or extensibility of adherends is likely to influence the strength of joints made with fairly hard adhesives in no mean degree. See also this Chapter 3, p. 81-82.

Taking the same joint as described above, if the strips are heavy, they will not be stretched to any marked extent when the joint is pulled apart. In other words, in this case the pull on the left strip is evenly taken over as a proper shearing-stress by the whole borderline between adherend and adhesive. When the thickness of the strips is reduced, a moment will come when the strip is decidedly stretched before the joint fails. The extra stress referred to in a tangential direction on the outer part of the border of the glue line and adherend is now set up and the breaking strength of the joint

decreases according to y . As this point will, however, depend on the extensibility of the strips, two strips of equal dimensions but of different coefficients of elasticity will behave differently. If the adhesion is adequate in both cases, the adhesive being sufficiently rigid (high elasticity modulus), it will be found that the stronger material will produce the stronger joint; for as a rule the strength of a material (*e.g.* a metal) runs parallel to its elastic modulus.

The work of J. W. MCBAIN and W. B. L. LEE⁵¹ is relevant at this juncture (see Fig. 48, Chapter 4 by C. MYLONAS and N. A. DE BRUYNE). This Figure shows the influence of the nature of the adherend on the strength of the joint, which corresponds to the mechanical constants of the materials joined, increasing with their tensile strength and elasticity modulus. Joints between nickel surfaces are stronger than those between aluminium. These results, which were obtained by the authors just mentioned, bear out the arguments advanced above.

Generalizing on the elasticity of adhesives, it may be said that the elastic modulus of an adhesive in the set, *i.e.* fully hardened, state should always be lower than that of the adherends. In this case the parallel stresses referred to are always lower.

(c) *Expansion and Movements of Adhesive Layers through Adsorption of Fluids*

This is a prime factor affecting the rheological behaviour of adhesives. Water is present everywhere in this world's atmosphere and almost all constructions containing non-metals are influenced by it. The relative humidity in our climate varies from 60–95 %, the water content of materials like wood, paper, etc., changes with the relative humidity of the atmosphere with which it is in equilibrium (See Fig. 32). The great affinity of these common materials for water is due to the large number of hydroxyl groups in their chemical structure. Now the occurrence of free OH groups in our most common non-metallic materials is no mere coincidence, the presence of strong polar groups in organic materials being one of the simplest and most usual means of sustaining strong cohesion in such materials (See Chapter 2 of this book by A. J. STAVERMAN). Organic materials without polar groups may be strong, if their molecular structure is three-dimensional. In materials of that kind molecular units are connected by direct atomic bonds to more than two other units. Materials like bakelite or vulcanized rubber are insoluble. Strong organic materials may alternatively be built up by the crystallization of linear molecules (*e.g.* polythene,

unvulcanized rubber, paraffin wax); but the strength of the materials of this group never reaches the value of three-dimensional materials, nor that of polar substances. Both groups are soluble, the non-polar ones in non-polar solvents, the polar ones in polar solvents. It may be said of both

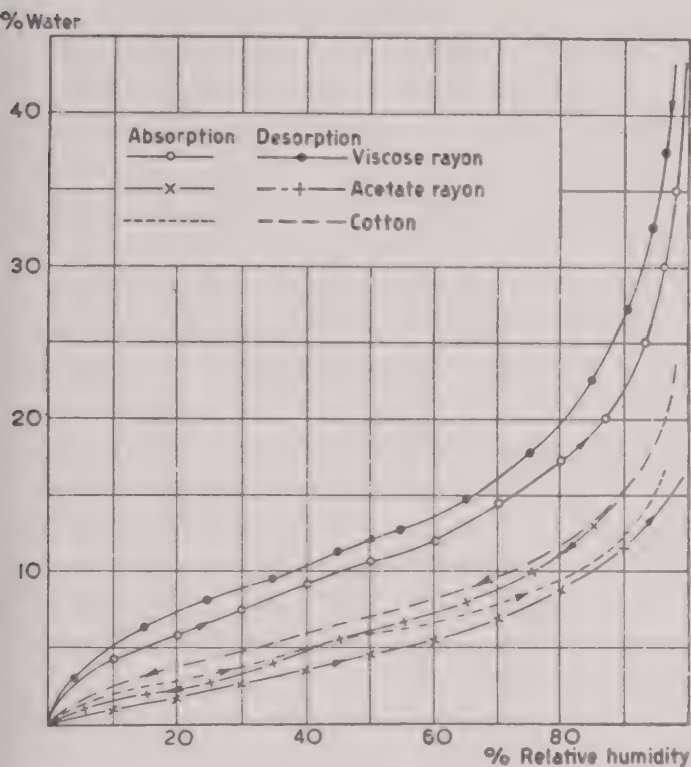


Fig. 32. Absorption and desorption of water by textiles as a function of the relative humidity.

substances. Crystallization means that a regular pattern is formed; usually *all* the polar groups of one molecule interact with all the polar groups of other members of the crystal or crystallite. This is impossible if these spaghetti-like molecules are arrayed at random. For this reason, the polar bonds between the molecules become far more effective upon crystallization and, as a result, the substances are insoluble even in strongly polar solvents (*e.g.* cellulose, wool).

The choice of organic material for adhesives subjected only to low stresses is almost unlimited (see section on plastic adhesives), but is confined

classes that the strength of these materials increases with increasing length of the molecules (up to a certain limit, above which the strength remains practically constant at higher molecular weights). The strongest high molecular weight materials consisting of linear molecules are those which contain polar groups and are crystallized as well. Crystallization of long molecules is fostered considerably by their orientation*.

Crystallized polar high polymers of this type mostly form fibrous

* Without orientation, crystallization of linear high polymers can only take place over a number of small areas, where a number of molecules are lying parallel by accident and form small crystallites. These molecules do not take part in such a crystallite over their whole length, but only partly; one molecule may take part in more than one crystallite.

to substances of high molecular weight, preferably crystallized, if greater strength is required. For adhesives called upon to match the mechanical properties of strong materials, we have to turn to polar substances*.

It is therefore clear that with strong adhesives considerable adsorption of water vapour in humid atmospheres is by no means rare. This is the case with all protein glues and also with dextrine and many synthetic adhesives containing free hydroxyl groups. The effect of such adsorption is twofold. The adhesive layer expands and tangential forces are set up on the boundary. At the same time, the rheological properties of the adhesive change. As these polar substances have strong forces between the molecules, these molecules will not slip past each other before a limit of shearing stress has been exceeded. They exhibit a pronounced yield value. The adsorption of water increases the average distance between the molecules; water molecules find a place between these molecules and saturate part of the strong electrostatic forces of the hydroxyl (or other polar) groups. The yield value is therefore lowered.

Thus, together with the expansion of the adhesive layer, its yield value is lowered. The deformability of the joint is increased and, if no mould or bacterial disintegration of the adhesive sets in, the joint will not fail, though its breaking strength may be reduced**. But what will happen, if the opposite event occurs and water escapes from the polar adhesive into a dry atmosphere? There will be contraction and the yield value of the adhesive layer will increase. This is very dangerous. Either of two things may happen: the adhesive may become brittle and break under slight but sudden mechanical impact, or the tangential forces at the boundary may exceed the limit of adhesion and the layer may break away from the adherend.

(d) *Internal Stresses built up in the Adhesive*

We have already considered some sources of inner stresses in the adhesive layers, *viz.*, outer forces (in connection with elasticity), adsorption of water from the outside. But the stresses often come from within, initiated by changes inside the adhesive. Once again, this will only have serious consequences if the yield value is high and the elasticity inadequate; in other words, in the case of strong adhesives.

The occurrence of internal stresses is mostly related to the mechanism

* The choice of polar substances as adhesives for polar materials is also indicated because no adhesion can be expected in the opposite case (see Chapter 2 of this book by A. J. STAVERMAN).

** In a few cases, as in that of adhesives like chlorinated rubber on glass, humidity may damage the adhesion, because water molecules get into the borderline between adhesive and glass.

by which the adhesive hardens. This hardening has been described in § 2(b,f.).

As has been stated, adhesives which harden by drying often hold back a certain amount of solvents for long periods. It may take months before these traces have disappeared, especially when the adhesive is sandwiched between adherends with low permeability for these solvents. As was stated in § 2, such solvents have a very strong plasticizing power.

While the apparently dry adhesive (containing a trace, say 5%, of solvent) is a strong, deformable solid, therefore, loss of solvent often converts it, with contraction, into a brittle, glass-like substance. Thus a joint may fail on ageing. Other adhesives may oxidize and contract as a result of this process (adhesives containing drying oils).

The chemical hardening discussed in § 2 (f) may be a very slow, prolonged process, sometimes causing strong stresses to be set up in the layer.

(e) Influence of Temperature on the Properties mentioned

The influence of temperature on the properties of adhesives as considered in the foregoing sections has been mentioned in the course of our discussions. A few general remarks on the rheology of hardened adhesives as influenced by cold and heat will therefore suffice here.

Cold is a serious menace to plastic adhesives, because it temporarily deprives them of their deformability. Nor can they withstand heat. Highly elastic adhesives are vulnerable to extreme cold, which converts them to rigid, often brittle substances. Very rigid adhesives are not as a rule much influenced by temperature, but if their coefficient of thermal expansion differs very considerably from that of the adherends, stresses will be set up on the border-line by changes of temperature. In the case of metals joined by glass enamels, or ceramics or glass joined in the same way, this difference in thermal expansion is the all-important factor. It is well known that glasses produce a nick in their expansion temperature curve, near the point where the glass shows the first signs of softening. A special metal is often chosen (*e.g.* Fernico, consisting of iron with 28 parts Ni and 18 parts Co) to ensure stable joints. This also shows a nick in its thermal expansion curve, at 440° C. ⁷².

Adhesives naturally absorb very much less water at higher temperatures; it should be borne in mind that this is hardly the case if the relative humidity is kept constant while the temperature is increased.

Contraction of adhesives, due to a slow loss of solvent, or by a slow process of chemical hardening, is very much increased by rising temperatures. As at the same time the rheological properties of such an adhesive

are influenced by increased temperature (lowering of viscosity and of yield value), it is impossible to say what the results will be in such cases.

§ 4. BRITTLINESS

A few remarks on brittle adhesives may fittingly conclude this Chapter on the rheology of adhesives.

What is brittleness? A material may be called brittle if it is fractured by moderate stress of very short duration. A light tap may break the material, whereas a load gradually applied can be increased to a heavier weight without causing fracture. Brittleness is related to absence of relaxation. Going from highly viscous, via plastic towards brittle materials, one sees that in the first case all internal stress is immediately neutralized by inner flow, whereas no such flow occurs in the brittle material. On closer examination, however, this viscous-plastic-brittle sequence proves to be illusory; for, a good many brittle materials are viscous, without having a yield value, of which pitch and cumarone resins are good examples. It is surprising to find that over-cured rubber is among the brittle substances.

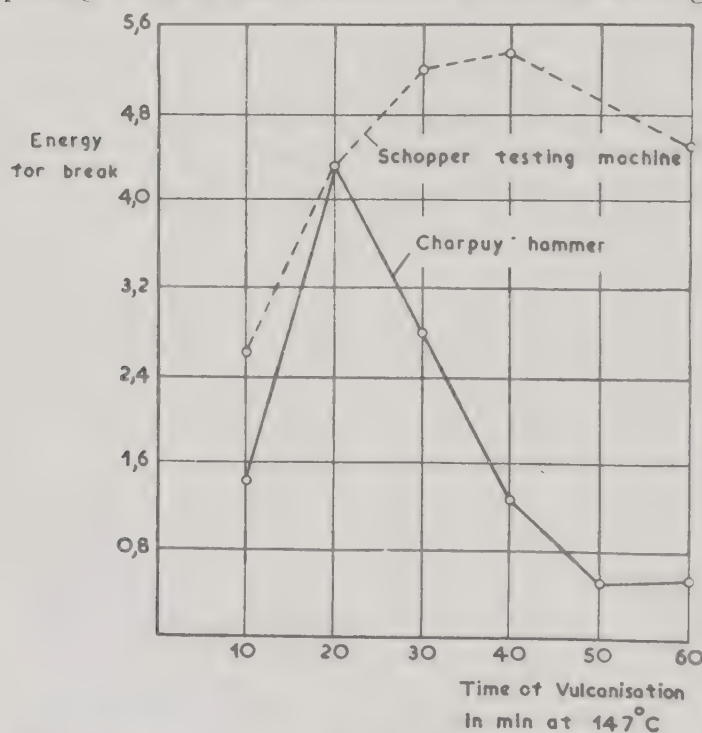


Fig. 33. Breaking strength of cured rubber mixture related to time of vulcanisation.

Comparative results with Schopper tensile tester (slow test) and Charpuy impact hammer (quick test).

From A. VAN ROSSEM and H. J. BEVERDAM, *Kautschuk*, 6 (1930) 225.

Over-cured rubber may be very strong and highly elastic; but it breaks immediately if stretched quickly.

Fig. 33, taken from a publication by A. VAN ROSSEM and H. J. BEVERDAM⁷³, shows clearly that the energy required to break a sample of cured rubber depends greatly on the speed at which the sample is stretched. This Figure reproduces curves for mixtures of F. L. Crepe (100 parts), Sulphur ($7\frac{1}{2}$ parts) and diphenylguanidine as accelerator (1 part), cured at increasing times of vulcanisation. The cured

samples were tested in two different ways: at slow speeds of stretching, as customary in rubber testing (Schopper tester) and at high speeds with an impact tester (Charpuy hammer). We can see from the results of Schopper tests in Fig. 33 that the rubber mixtures received their optimum vulcanization after 30 minutes and were decidedly over-cured after 50 minutes at 147° C. The difference in energy at break is only to be found in fully cured and especially in over-cured samples.

This behaviour of cured and over-cured rubber may explain the behaviour of soft and brittle materials in general. Let us consider again a piece of material consisting of long intertwined and partly mobile molecules. We saw that this is the picture both of natural and of synthetic rubbers. Let this piece of material be suddenly stressed in one direction. Strain will be set up and it is clear that in the interior of this sample a small number of molecules or parts of molecules will absorb most of the stress at its very onset. This must be so, because nearly all stressed parts of molecules are able to yield to the sudden stress by a slight rotary movement, the only exception being those parts of molecules which were oriented precisely in the direction of the applied stress. At this first moment sections of the long molecules will be much more liable to change their direction than to glide past their neighbours, for those sections of rubber molecules are free to change direction, almost as freely as in a liquid (they show low micro-viscosity), but offer considerable resistance to the relative movements of whole molecules (macro-viscosity).

If, however, these highly stressed parts of molecules move slightly in a longitudinal direction, this will set up some movement within the material, placing a number of other molecules in the same position as the first ones. In this way the stress is distributed among a large number of directed molecules, no cleavage will take place and the material will not be brittle. It will be brittle, however, if no such slight internal movement is able to take place, owing, for example, to abrupt imposition of stress.

This behaviour is clearly demonstrated by the over-cured rubber mixes studied by VAN ROSSEM and BEVERDAM and shown in Fig. 33.

Brittleness disappears if somewhat more time is taken to build up the applied stress (Schopper test), as during that time the straining of carbon against carbon chains causes slight flow or dislocation of their immediate environment. Thus these "direct chains" are partly released and other chains come into action. Extension of cross-linking between the molecules by increased time of vulcanization, however, impedes the gliding of stressed and directed molecules past their neighbours, with the result that brittleness sets in.

Any brittle material not possessing rubber-like elasticity, but highly viscous in its behaviour, presents a similar picture. Pitch is an example, in which likewise a few "direct chains" will be stressed, though by far less deformation, owing to poor elasticity. Nevertheless, lack of opportunity for the viscous displacement of sections of molecules within the material will concentrate the total stress in a similar manner at a few vulnerable points.

With this same picture before us, we can readily see that all materials debarred from internal flow must inevitably be brittle, since no opportunity is afforded for homogeneous internal distribution of an applied stress. As no material is entirely homogeneous, some part of an absolutely hard body will be more stressed than others and breakdown will start at the over-stressed point, because this uneven distribution of stresses cannot be corrected by internal flow in the near-instantaneity of sudden impact, which deprives the material of all deformability. Once break-down has started, the very strong notch effect obtaining in hard bodies will complete it in a fraction of a second.

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CHAPTER 4

STATIC PROBLEMS

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PART I. THEORETICAL INVESTIGATION OF THE STRESSES IN JOINTS

§ 1. INTRODUCTION

External forces seldom produce a uniform field of stress even in a homogeneous body; when the body consists of two or more materials joined together, as for example in a glued joint, a state of uniform stress is quite exceptional. The difference of physical properties at either side of the interface between adhesive and adherend will produce a varying intensity of stress, hence will introduce some degree of stress concentration (ratio of highest to mean stress).

Failure to recognise the significance of such stress concentrations has in the past led to some confusion and to erroneous conclusions. Thus it has been customary to express the strength of a glued joint as an average breaking stress, *i.e.*, the breaking load divided by the glued area and expressed in pounds per square inch or kilograms per square millimetre. It was later found that the stresses developed in the glue layer are not uniform, the stress concentration depending on the shape and size of the test specimen so that the more highly stressed areas break first and limit the strength of the whole joint.

The exact knowledge of the stress distribution in glued joints is therefore indispensable for the prediction of their strength; it is also a necessary element in the study of the behaviour of the adhesive.

This chapter is mainly confined to stress distributions below the elastic limit but a paragraph at the end deals briefly with the effect of plastic flow. This is not a very serious limitation because the adhesives are mostly brittle, breaking with little or no creep.

§ 2. TORSION JOINTS

The simplest stress distribution occurs with joints subjected to pure shear, as happens with the two circular co-axial thin walled cylinders of Fig. 34

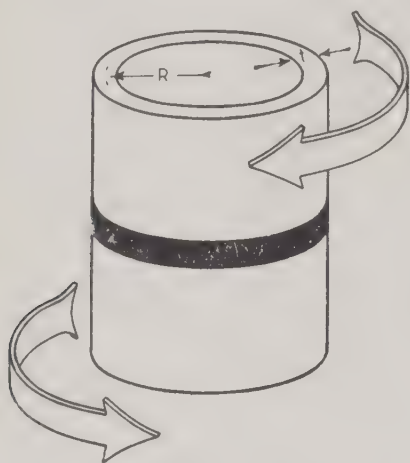


Fig. 34. Thin-walled metal cylinders joined end to end and subjected to torsion. The adhesive is in a state of pure shear.

which are joined end to end and subjected to torsion. Then the adhesive, as well as the walls of the cylinders, will be under pure shear equal to the applied torsional moment M divided by the glued area and by the mean radius of the cylinder:

$$\tau = \frac{M}{2\pi R^2 t} \quad (1)$$

This shear stress is the same throughout the joint and for this reason such joints break at high loads; "Redux" joints between mild steel cylinders, give failing stresses of the order of 8,000 p.s.i. in shear. This limit is much greater than the apparent mean shear strength of lap joints, because as will be seen, the latter

develop peak stresses at each end of the overlap.

It should be noted that for the torsional joint, the radial strain (change in thickness t) is zero and therefore whatever the elastic constants of adherends and adhesive, there will be no radial stress due to differential radial strain.

§ 3. BUTT JOINTS

A striking example of non-uniform stress is provided by a layer of an elastic adhesive subjected to tension or compression between two parallel flats. It might at first be supposed that the stress, like the applied normal strain, is the same everywhere in the layer. This would happen only if, under the action of the normal stress, neither the plates nor the adhesive tended to deform laterally or did so by the same amount, in other words if the ratio $\mu : E$ of Poisson's ratio to YOUNG's modulus were the same for both materials. Thus for example the stress distribution will obviously be uniform when layer and flats are of the same material. It will again be uniform if the flats are of a very hard material like steel and the layer of a much softer material but having a proportionally lower Poisson's ratio,

as for example cork, which shows hardly any lateral expansion when compressed: for both materials $m : E \simeq 0$ and the stress should be uniform.

This condition is seldom, if ever, fulfilled in practice where the ratio $m : E$ is usually higher for the adhesive layer than for the butt-joined adherends, so that the tendency for lateral deformation will be unequal in the two materials. In regions distant from any edge the material of the layer is laterally restrained and accordingly lateral stresses will develop; in regions near the edges and on the free edges themselves the material of the layer is not supported laterally. The only restraint is imposed by the adhesion on the interfaces on which shearing stresses will develop. Near the edge the normal stress can reach a considerably higher value than in the centre areas, or, otherwise expressed, a stress concentration will develop near the edges. The plane problem of a plate compressed or pulled along two parallel edges by two perfectly rigid plates to which it firmly adheres has been solved approximately by TIMOSHENKO¹ who used polynomials and gave a numerical solution for a square plate, and by WITTRICK and HOWARD² who developed a relaxation method for mixed boundary conditions, *i.e.* where boundary conditions are specified in some part as stress conditions and in others as displacement conditions, and applied it to a rectangular plate of length $2\frac{1}{2}$ times its width pulled lengthwise. Both solutions confirm the existence of a high stress near the corners of the plate, but both are of increasing inaccuracy as they near these points, the relaxation method breaking down completely there.

§ 4. SIMPLE LAP JOINTS

The commonest type of joint is the lap joint in which two sheets overlap and are fixed together by a layer of adhesive between them. Loading in the plane of the sheets produces varying shearing and tearing stresses in the adhesive as well as on the glued faces and in the material of the sheets. The joint may fail either in the adhesive or on an interface or even in the joined members according to the highest stresses developing at each of these parts and to the strength of adhesive, adhesion and adherends. The interfacial adhesion of modern adhesives is high so that the failure mostly occurs either in the glue as, for example, with metal-to-metal joints, or in the adherends as happens with wood joints.

The stress is not uniform along a lap joint and the peak stress may be several times higher than the apparent or *mean stress*, defined as the load divided by the glued area. The peak stress and its ratio to the mean stress, in other words the *factor of stress concentration*, are markedly dependent on the geometrical proportions and the elastic constants of the materials of

the joint. Though the thickness of the glue layer is known to affect the ultimate strength of the glue, yet at present the strength of adherends and adhesive will be assumed constant and the strength of a joint will be taken to depend only on the peak stress. Before proceeding to calculate the value of this stress it is thought useful to give some evidence of its existence and some general idea of the behaviour of a lap joint under tension.

The breaking stress is found to be independent of the width of overlap but diminishes with increasing length of overlap. This was shown by

N. A. DE BRUYNE^{7,9}

in the diagram of Fig. 35 where the failing load and the apparent breaking stress of a simple lap joint made of two steel strips 1 in. wide and $\frac{1}{4}$ in. thick joined together by the Redux process, has been plotted against the length of overlap. The failing load is proportional to the overlap only as long as this is shorter than about $\frac{1}{2}$ in. but for

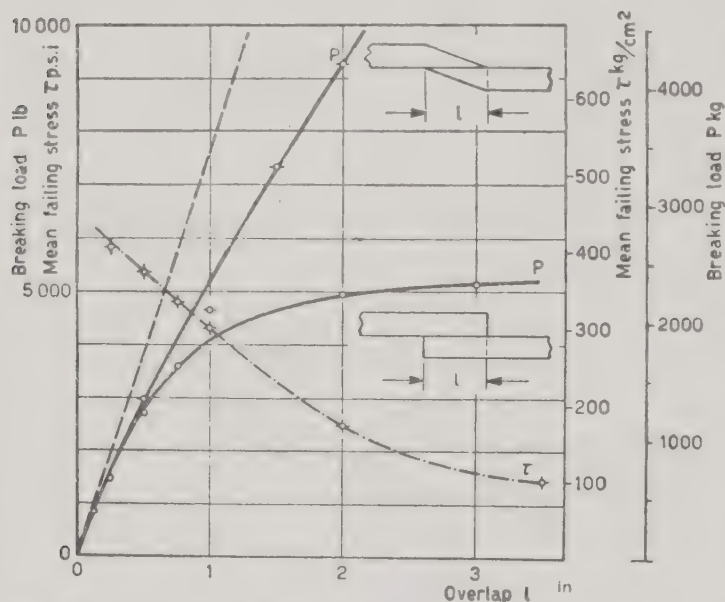


Fig. 35. Failing load P and mean failing stress τ of lap joints.

longer overlaps it tends to become constant while the apparent stress falls off considerably. Thus an increase in overlap from 1 in. to 2 in. raises the breaking load from 4300 lb. to only 5000 and reduces the apparent stress from 4300 to about 2500 p.s.i.

A similar behaviour has been noticed in side fillet-welded joints between steel plates, where the stress was not found to increase as expected when the overlap and the fillets were lengthened, as is explained in a review and general discussion of the strength of fillet welds by E. P. S. GARDNER³.

This behaviour is due to the concentration of stress at the ends of the overlap owing to two main causes, namely to the differential strain of the joined members and to their bending, as is explained below.

(a) Differential Strain

The stresses arising from the differential straining of the joined members

can be understood by the comparison between a joint with very stiff non-deformable members and one with extensible, though non-bending members. In both cases the adhesive layer is taken of exaggerated thickness for purposes of demonstration.

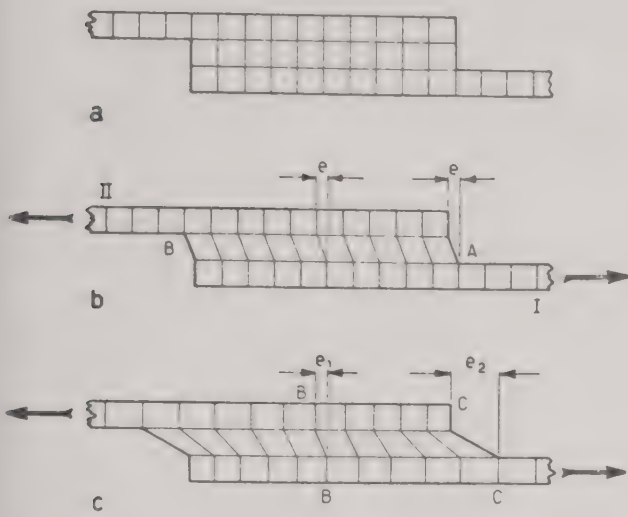


Fig. 36. Schematic explanation of the shearing in the adhesive: (a) unloaded lap joint, (b) loaded joint with inextensible adherends, (c) joint with elastic adherends.

ally diminish towards B where it will be zero. On the contrary the stress of the member II will be highest at B and diminish to zero at A . Of course this variation of stress is unimportant as long as the members I and II behave as absolute solids, but if they are extensible and obey the laws of elasticity these members will develop strains proportional to the existing stresses. The picture of the deformation will be as in Fig. 36c and the originally corresponding points, B, C near the middle of the joint and D, E at the end will be displaced by unequal amounts e_1 and e_2 respectively, the end displacement being considerably larger, and therefore resulting in a higher stress in the adhesive at each end of the overlap. This

has been confirmed by various tests which showed that the failure starts at

purposes of demonstration. (Fig. 36a). The non-deformable members will move as solid blocks and the adhesive will suffer shear strain and deform so as to accommodate the displacement e of the members (Fig. 36b), which will be the same throughout the joint. But each member bears the full load P just before the joint and transmits it gradually to the other through the adhesive. Thus the stress of member I will be highest at A and gradually

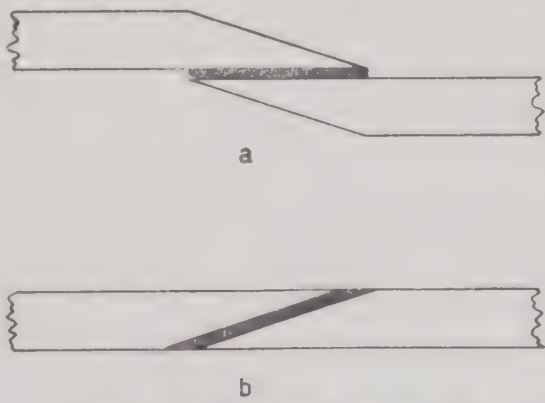


Fig. 37. (a) Tapering lap joint, (b) scarfed joint.

the edge of the joint ⁴. The above are also confirmed by the higher strengths of joints with tapering members (Fig. 37a and 35), where the differential strain and the resulting stress concentration at the edges are considerably reduced. The cross-section of each member diminishes as the load borne by each member, thus producing almost constant stress and strain throughout the overlap and resulting in equal and smaller displacements. This has been proved by extensometer readings as well as tests to destruction ⁵ which showed that the joint efficiency *i.e.* ratio of apparent breaking stress to the strength of the adhesive, could be raised to 80% by the use of scarfed joints (Fig. 37b). The tensile stress component which then develops in the adhesive can be kept small by splicing at a sufficiently small angle. Nevertheless it should be noted that this increase in strength might be due to the central loading and the subsequent absence of bending, such as is examined in the next paragraph.

(b) Eccentricity of Loading

The members of a lap joint are necessarily offset by at least their thickness s (Fig. 38a), and the line of pull joining the points of application of the loads P will

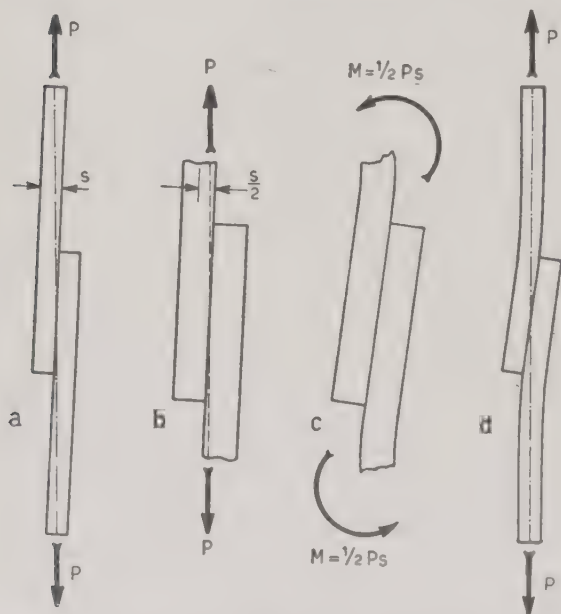


Fig. 38. Schematic explanation of the bending of the adherends and of the resulting tearing stresses at the ends of the overlap:

- (a) Lap joint before the deformation.
- (b) Eccentricity of loading near the overlap.
- (c) Bending moment near the overlap.
- (d) Final deformation of the joint.

be oblique and pass through the midpoint of the joint. Just before the beginning of the overlap the line of pull will be along the inner face of each member (Fig. 38b), provided of course that the length of each member beyond the joint is considerably larger than the overlap. The eccentric loading of each member will give rise to a bending moment $M = \frac{1}{2}Ps$ (Fig. 38c) which will tend to pull the members apart. Under this moment the members, if long enough, bend and the joint distorts as in Fig. 38d. This deformation reduces the tearing stresses because, when thus deformed, the line of pull is nearer to the central axis

of each member and therefore the bending moment is less. Thus it is seen that all by itself the joint assumes the least strained position, or in other words deforms to the shape involving the least amount of strain energy.

The stresses developing in this way are tensile and normal to the interface, and are called "tearing" or "peeling" stresses; they are confined to the areas adjoining the ends of the overlap and may considerably reduce the strength of lap joints. The tearing stresses have been long overlooked in the calculation of joints but are fully considered by GOLAND and REISSNER (see § 6).

§ 5. VOLKERSSEN'S ANALYSIS OF LAP JOINTS ⁶

This analysis is concerned only with the stresses arising from the differential straining in lap joints and does not examine the tearing stresses resulting from the bending of the members. The bonded members are assumed to be in pure tension and shear stresses are examined in the adhesive layer only, their maximum being found at each end of the overlap. The adhesive layer is assumed of uniform thickness and its ends are plane and normal to the direction of application of the load.

For materials of Hookean elasticity the factor n of stress concentration — ratio of maximum shear stress to mean or apparent stress — is found to be:

$$n = \frac{\tau_{\max}}{\tau_a} = \sqrt{\Delta/W} \frac{W - 1 + \cosh \sqrt{\Delta/W}}{\sinh \sqrt{\Delta/W}} \quad (2)$$

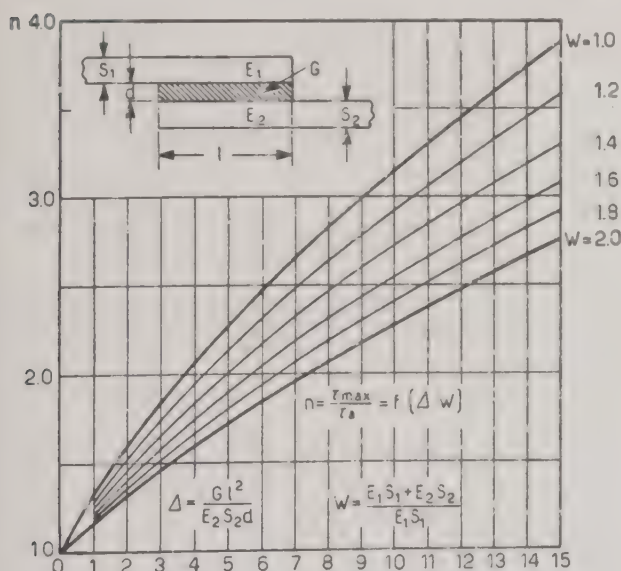


Fig. 39. The factor of shear stress concentration of lap joints as a function of Δ and W .

* The graph for the inverse quantity $\frac{1}{n} = \frac{\tau_a}{\tau_{\max}}$ is given by N. A. DE BRUYNE ⁷

where:

$$\Delta = Gl^2/E_2 s_2 d \quad (2a)$$

$$W = (E_1 s_1 + E_2 s_2)/E_1 s_1$$

and E_1 , E_2 and s_1 , s_2 are the YOUNG'S moduli and thicknesses of the adherends and G , d the modulus of rigidity and thickness of the adhesive layer as in Fig. 39.

Formula (2) has been put in the form of a graph* (Fig. 39) which gives the factor n in terms of Δ for various values of W . The ratio of maximum to ap-

parent shear decreases rapidly with Δ . For the limiting case of $\Delta \rightarrow 0$, $\tau_{\max.}/\tau_a \rightarrow 1$ and the shear stress is uniform throughout the joint. For members of the same size or of thickness inversely proportional to their YOUNG's moduli W reduces to 2 and (2) can be written:

$$n = \frac{1}{2} \sqrt{2\Delta} (\coth \sqrt{2\Delta} + \sec b \sqrt{2\Delta})$$

or

$$n = \sqrt{\Delta/2} \coth \sqrt{\Delta/2} \quad (3)$$

or otherwise:

$$n = f(\Delta)$$

Thus it is seen that the factor n of stress concentration is a function of a single dimensionless coefficient Δ , which therefore is the factor of similarity for the comparison of lap joints. For the comparison between joints of the same material and glued under the same conditions, N. A. DE BRUYNE⁷⁻⁹ uses the "joint factor" $|s|/l$ which is simpler than Δ but has the dimension of (length)⁻¹ and its value depends on the units used; yet it is most useful when the thickness d of the adhesive is unknown in absolute magnitude, though it is known to be the same owing to the similar conditions of gluing.

§ 6. THE THEORY OF GOLAND AND REISSNER¹⁰

In spite of a few simplifications and approximations this is the most rigorous mathematical study of the stress distribution in glued joints and it is considered useful to review it fully. Though the concluding formulae for the calculation of the stresses are rather too complicated to be of practical use, yet their graphical representations are simple and could be used in practice with great advantage.

The deformation of the glued members beyond the joint is calculated by the finite deflection theory of cylindrically bent plates and characterised by the ratio k of the existing bending moment just before the joint, to the value of this moment for inflexible members:

$$\frac{1}{k} = 1 + 2 \sqrt{2} \tanh b \left\{ \sqrt{\frac{3}{2}(1-n^2)} \cdot \frac{l}{2s} \sqrt{p/E} \right\} \quad (4)$$

where

E, n = YOUNG's modulus and POISSON's ratio of members

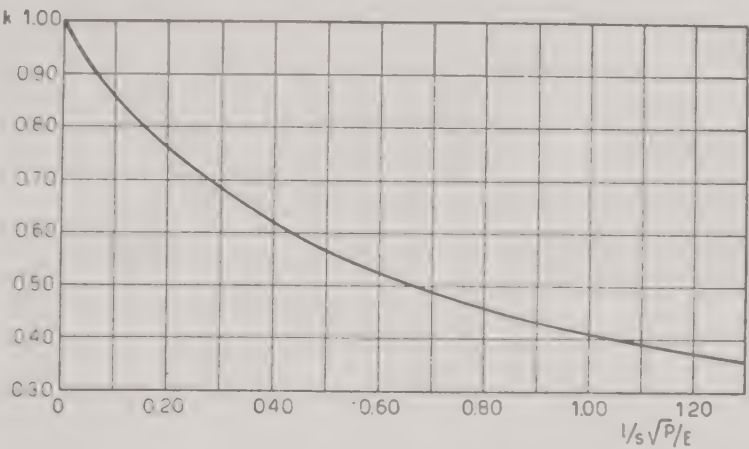
l = length of overlap

s = thickness of either member

p = mean tension of members away from overlap.

The dimensionless factor k which appears in all the stress formulae depends

on the geometrical proportions of the joint (*i.e.*, *l* and *s*) as well as on the elastic properties (*i.e.*, *E* and *n*) of the members, but also on the tension *p* of the members, and therefore changes with the load. The value of *k* is unity for undeformed members either because of their stiffness or because of the small load applied. For increasing flexibility or load, *k* diminishes tending towards zero as a limit, though in practice it remains above 0.35 as is shown in Fig. 40.



Courtesy of Goland and Reissner¹⁰
Fig. 40. Graph of the factor *k* characterising the extend to which the adherends bend.

Once the deformation of the joined members and the resulting stresses are known just beyond the beginning of the overlap, the stress distribution in the joint itself is calculated as a problem of plain strain for the extreme cases of adhesive layers too thin and stiff to affect the flexibility of the joint, as well as of thick deformable layers which are the main cause of flexibility. If *d* is the thickness of the adhesive layer, *s* the thickness of either member and *E*, *G* and *E_a*, *G_a* are the YOUNG'S and shear moduli for the members and adhesive respectively, then the first case is specified by the conditions:

$$\frac{d}{E_a} \lesssim \frac{1}{10} \frac{s}{E} , \quad \frac{d}{G_a} \lesssim \frac{1}{10} \frac{s}{G} \tag{5}$$

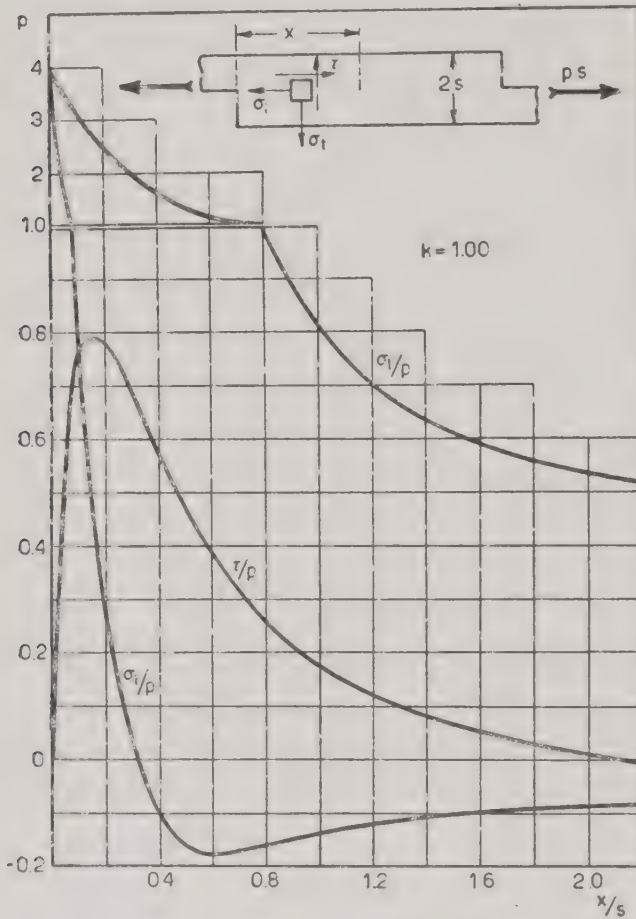
and refers mainly to wood-to-wood joints, while the second concerning mainly metal-to-metal joints and gap joints, is characterised by the conditions:

$$\frac{s}{E} \lesssim \frac{1}{10} \frac{d}{E_a} , \quad \frac{s}{G} \lesssim \frac{1}{10} \frac{d}{G_a} \tag{6}$$

(a) *Thin Adhesive Layers*

The existence of the layer itself is disregarded, the whole joint being considered as consisting of a continuous homogeneous material and the calculated stresses are those of the members, though along the glue line

they can be assumed to be equal to those of the adhesive layer. Yet this assumption is not indispensable as this part of the present analysis refers mainly to wood-to-wood joints which, when joined with the modern synthetic adhesives, always fail in the wood and not in the adhesive, so that the highest stress in the members is more interesting than the highest



Courtesy of Goland and Reissner¹⁰

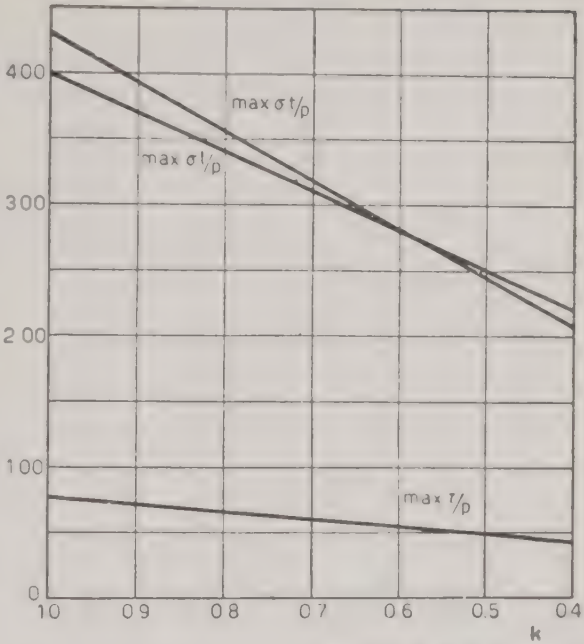
Fig. 41. Longitudinal and transverse tension and shear stress as functions of the distance from the edge of the overlap for $k = 1$.

edge both σ_t and σ_c are highest (4.3 and 4 respectively times higher than the mean member tension p), while the shear stress is zero but rapidly increases to a maximum of about $0.8 p$ within a distance of $0.15s$ from the edge and diminishes to zero again at about $2s$. The peak values of these stresses are considerably affected by the bending of the members (value of k) and Fig. 42 gives their variations as functions of k . With increasing member tension p the value of k and of the maximum ratios $\frac{\tau}{p}$, $\frac{\sigma_t}{p}$, $\frac{\sigma_c}{p}$ decrease.

stress in the glue. Of course all glues are not as strong and then the highest stress in the adhesive determines the strength of the whole joint.

The values of the shear stress τ and the tearing stress σ_t in the glue as well as the longitudinal tension σ_c of the innermost member fibre are given as converging series. Their ratios to the mean member stress p as they vary along the glue line are shown in Fig. 41 for the special case of $k = 1$ (rigid members). The highest stresses are confined within a distance from the edge equal to about twice the thickness s of the members. At the very

Thus a change of k from 1.0 to 0.4 reduces σ_t from $4.3p$ to $2.1p$ and τ from $0.8p$ to $0.45p$, though of course the absolute values of these stresses increase with p . It is found that the stress distribution and the values of the peak stresses are independent either of the relative dimensions of the joint or of the physical properties of the adhesive. Thus for joints with thin inflexible adhesive layer the stress concentration is confined around the ends of the overlap and its magnitude depends only on the value of k .



Courtesy of Goland and Reissner¹⁰

Fig. 42. Reduction of the stresses resulting from the bending of the adherends (diminishing value of k).

(b) Flexible Adhesive Layer

In joints with a relatively flexible adhesive layer, for example in metal-to-metal joints, both the shear and the tearing stresses have their maximum values at the edge of the overlap. The shear - stress - concentration factor n (ratio of maximum shear τ_{max} to mean shear τ_m) can be put under the form:

$$n = \frac{1 + 3k}{4} \sqrt{2\Delta} \coth \sqrt{2\Delta} + \frac{3}{4} (1 - k)^* \tag{7}$$

which is reminiscent of formula (2) found in the simplified way of VOLKERSEN. The factor n is again a function of Δ but k is also introduced to take account of the effects of the bending:

$$n = f(\Delta, k) \tag{7a}$$

The variation of n with Δ for various values of k is given in the diagram of Fig. 43 which is simpler than the corresponding graph given by GOLAND and REISSNER¹⁰. As in VOLKERSEN's analysis the shear stress is uniform ($n = 1$) irrespective of the value of Δ as long as this is smaller than about

* Found from the corresponding formula of GOLAND and REISSNER by introducing the shear stress instead of the mean tension p , and the factor Δ given in formula (2a).

0.1, but the stress concentration increases rapidly for higher values of Δ and for $\Delta \gtrsim 2$ becomes practically proportional to Δ (curves become straight lines). In fact for $\Delta \gtrsim 2$ formula (7) can be simplified¹⁵ to:

$$n \simeq \frac{1}{4}(1 + 3k) \sqrt{2\Delta} + \frac{1}{4}(1 - k) \quad (8)$$

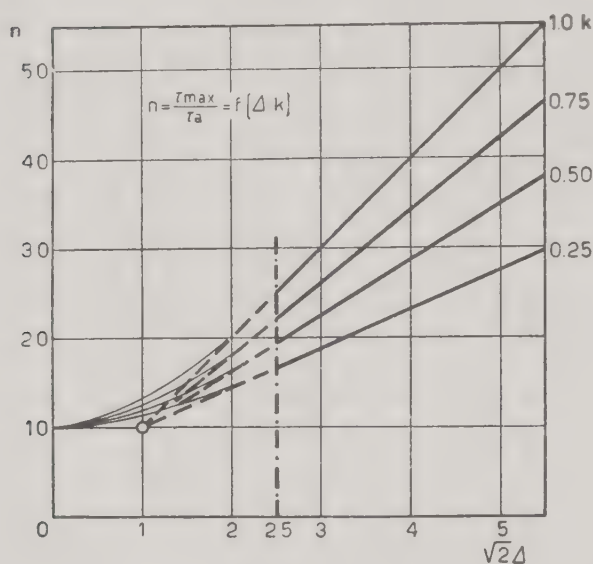


Fig. 43. The factor n of shear stress concentration in lap joints as a function of Δ .

The bending of the members (k small) is seen to have a reducing effect on the highest stresses.

The maximum tearing stress σ_{\max} developing at the edge of the overlap is found in terms of the mean tension p of the members as a function of l/s , k , and γ , where γ is a factor depending only on the relative flexibilities of members and glue layer:

$$\gamma^4 = 6 E_a s / E d \quad (9)$$

$$\text{and } \sigma_{\max} = p f_1(l/s, k, \gamma) \quad (10)$$

GOLAND and REISSNER¹⁰ give a graph of this formula for various values of k , using as abscissa the products $\gamma l/s$. If, however, $(\gamma l/s)^2$ is taken as abscissa the graph becomes as in Fig. 44; although l/s does not cancel out of (10), yet the graphs consist of almost straight lines, at least for $(\gamma l/s)^2 \gtrsim 20$. C. MYLONAS¹⁵ found that the approximate simplified formula will be:

$$n_1 = \sigma_{\max}/p \simeq \frac{1}{2} k \gamma^2 \quad (11)$$

This formula is of considerable interest since it presents the factor of tearing stress concentration n_1 as a function only of k and γ and therefore independent on the overlap l except in so far as this is contained into k ; in other words the overlap l influences the tearing stress only by affecting the deformation of the members. For increasing load the factor k and therefore n_1 diminish, though σ_{\max} increases in magnitude but slower than the load.

* A better value would be $(0.485 k + 0.015) \gamma^2$ giving an error of less than 1 %, yet $\frac{1}{2} k \gamma^2$ has the advantage of simplicity, is absolutely correct for $k = 1$ and introduces an error increasing up to at most 4 % for $k = 0.4$.

For the comparison of the relative intensities of shear and tensile stresses C. MYLONAS¹⁵ found it useful to relate the tearing to the shear stress and introduced the factor n_2 of tearing stress concentration as the ratio of the maximum tearing stress σ_{\max} to double the mean shear τ_m

$$n_2 = \frac{1}{2} \sigma_{\max} / \tau_m \simeq \frac{1}{2} k \gamma^2 p / (2 p s / l) = \frac{1}{4} k \gamma^2 l / s \tag{12}$$

Introducing the value of γ from (9) and substituting the shear modulus G_a to the YOUNG's modulus E_a of the adhesive with the help of the relation between the elastic constants:

$$E_a = 2 (m_a + 1) G_a ,$$

where POISSON's ratio m_a is taken as 0.33, it can be found that:

$$n_2 \simeq \frac{1}{4} k \left| \sqrt{\frac{16 G_a l^2}{E_a s d}} \right| = k \gamma \Delta \tag{12a}$$

A partial blending of the theory of VOLKERSEN with that of GOLAND and REISSNER is made in a paper by F. J. PLANTEMA¹¹ in which the differential strain of the

members (see Fig. 36) is calculated by the method of VOLKERSEN and formulae similar to (2) and (3) are found for the shear stress concentration at the edges of the overlap. This is followed by the calculation of the bending moment (Fig. 38c) and the resulting stress on the glued faces of the members at the edge of the overlap. The deformation of these

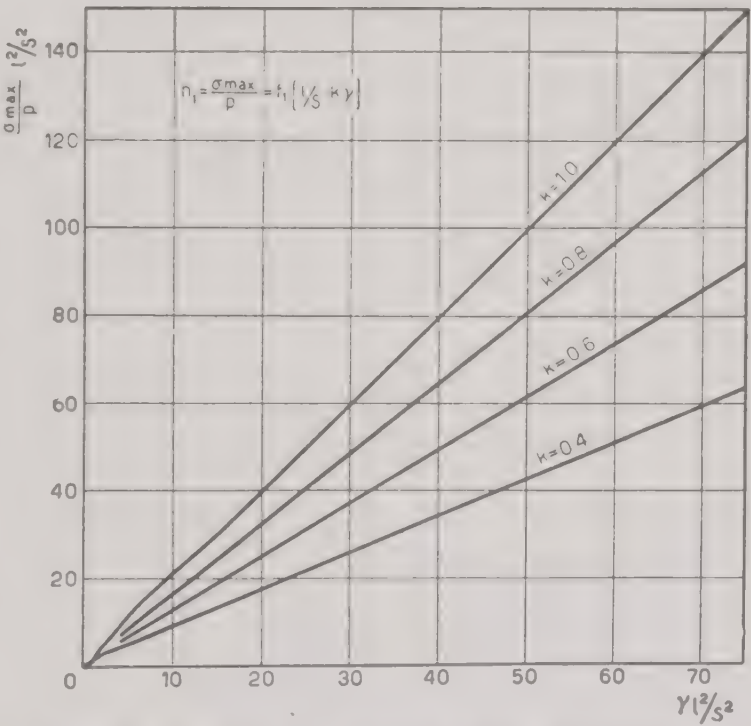


Fig. 44. The factor n_1 of tearing stress concentration.

faces of the members at the edge of the overlap. The deformation of these

members is then taken into account by introducing the factor k taken from GOLAND and REISSNER and the total differential strain of the members due to both tension and bending is used for the correction of VOLKERSEN's formula. From PLANTEMA's results the factor of stress concentration can be found as equal to:

$$n = \frac{\tau_{\max}}{\tau_m} = \sqrt{\frac{1}{2} \Delta (1 + 3k)} \coth \sqrt{\frac{1}{2} \Delta (1 + 3k)} \quad (13)$$

No calculation is made of the tearing (tensile) stresses.

A method of calculation similar to VOLKERSEN's is given by H. GRANHOLM in a recently published book¹² in which the same principles are used for the calculation of the shear strength of composite beams and columns. The only difference in this method is that a coefficient of deformation of the binding material (nails, wedges or corrugated rings) is used instead of the quotient G/d of the shear modulus by the thickness of the adhesive layer. This coefficient covers also the deformation of the joined members and is determined experimentally in each particular case.

The same method has been used by H. HOVGGAARD¹³ and H.W. TROELSCH¹⁴ for the calculation of the stresses developing in side-welded steel plates, the experimental coefficient being termed "detrusion ratio".

A full exposition and critical comparison of the various theories may be found in reference¹⁵.

§ 7. COMPARISON AND DISCUSSION OF THE RESULTS

The formulae for the shear stress obtained by VOLKERSEN, GOLAND and REISSNER for joints with flexible adhesive layers, and finally by PLANTEMA, are of the same type and can be easily compared. Noting by the subscripts V, GR and P, the factors of stress concentration found respectively by each of the three methods, we have for $k = 1$ (inflexible members):

$$n_V = \sqrt{\frac{1}{2} \Delta} \coth \sqrt{\frac{1}{2} \Delta} \quad (3)$$

$$n_{GR} = n_P = \sqrt{2 \Delta} \coth \sqrt{2 \Delta} \quad (14)$$

But for $\Delta \gtrsim 4$, $\coth \sqrt{\frac{1}{2} \Delta} \cong \coth \sqrt{2 \Delta} \cong 1$, and therefore:

$$n_V \cong \sqrt{\frac{1}{2} \Delta} \quad (16)$$

or

$$n_{GR} = n_P \cong \sqrt{2 \Delta},$$

$$n_{GR} = n_P \cong 2 n_V$$

and therefore for long joints ($\Delta \gtrsim 4$) the maximum shear as found by VOLKERSEN will be only half as big as calculated by the other two theories

(see also § 8 on double lap joints). For smaller values of Δ this difference diminishes and for $\Delta \lesssim 0.3$ all factors of shear stress concentration are nearly equal to unity, *i.e.* for very short joints the shear is uniform throughout the overlap.

A pronounced flexibility of the adhesive as compared with the adherends—*i.e.* E_a and G very small in comparison with E —also results in small values of Δ and γ and as such an adhesive cannot be very strong the applied loads will not be such as to produce a severe bending of the adherends and k can be taken as unity. Then the factor n is unity and n_1 is nil and therefore the adhesive will be uniformly sheared throughout its length and the strength of the joint will be proportional to the overlap. Such a good confirmation of the theories was experimentally obtained by tests on lap joints with the rubbery adhesive Pliobond¹⁶.

For decreasing k , n_{GR} and n_p diminish and differ. Their difference is stronger for high values of Δ . For diminishing k the difference increases and for $k \rightarrow 0$ (very flexible members):

$$n_p \rightarrow \sqrt{\frac{1}{2} \Delta} \coth \sqrt{\frac{1}{2} \Delta} = n_v \quad (17)$$

In other words for very flexible members PLANTEMA's results should coincide with VOLKERSEN's.

As a general rule the bending of the adherends has a reducing effect on the highest stresses, as can be seen in all the previous formulae and graphs which give smaller stresses for diminishing values of k .

In conclusion it can be summarised that in lap joints the highest stresses develop at either end of the overlap and that the ratios of these stresses to the mean stress are smaller, *i.e.*, the joint is stronger for:

- (1) Short overlap
- (2) Thick adherends
- (3) Thick adhesive layer
- (4) Low stiffness of adhesive as compared with the adherends
- (5) Easily bending members.

It is necessary to repeat that these are the results of a more or less rigorous investigation by the theory of elasticity and give the approximate highest developing stresses resulting only from the external loading and for adherends and adhesive which are isotropic and follow HOOKE's law, whereas the actual strength of the joint depends also on the existence of initial stresses and on the strength of the adhesive itself which appears to be influenced by the thickness of the layer (see § 12). Furthermore the elastic behaviour of both adhesive and adherends may be far from isotropic and Hookean, thus to some degree invalidating the theoretical results.

The effects of these factors on the strength of joints are discussed in the next paragraphs.

The results of these theories are not all compatible with the actual conditions in the adhesive layer. Thus all theories find a maximum shear stress on the very edge of the glue layer at each end of the overlap and yet this edge, being a free boundary, can develop only tangential tension or compression but no shear, which should be zero at this very place. This incompatibility arises from the assumptions on which the theories are based.

For thin inflexible adhesive layers GOLAND and REISSNER consider the joint as continuous and homogeneous and assume that the adhesive will be subjected to the stresses which develop along the glued plane, while for deformable adhesive layers they work on the same principle as VOLKERSEN, namely they calculate the stresses in the adhesive from the relative displacements of the joined members and the elastic properties of the adhesive by assuming that these stresses are constant within any cross-section, *i.e.*, do not vary in the direction of the thickness of the adhesive. In either case the results will be accurate in the inner parts of the joint, while in the areas near the ends of the overlap and in particular on the edge itself this method of analysis is bound to lead to inaccuracies. However small the thickness of the adhesive layer might be, it has to be taken under consideration for the stress distribution in areas distant by the same order of magnitude from the edge. The adhesive layer should be considered as a slab of the same thickness and loaded on either side by the stresses which are found along the glued plane. As was seen in the paragraph about butt joints, even simple tension or compression of such a slab between two undeformable flats does not create a field of uniform stress, the edges introducing considerable irregularities which extend to a depth of the same order of magnitude as the thickness of the layer. Similar irregularities will unavoidably appear along the edges of the adhesive layer at either end of the overlap and though extending to a very small depth should nevertheless considerably affect the strength of the joint since the highest stresses occur in that same area.

The effect of the edge is all the more difficult to find because its shape is unknown. By the photoelastic tests described later (see Part II § 5 and 6) the stress along a semicircular glue boundary is found to vary from tension on the one side to compression on the other, which confirms the expressed opinion that at least near the edges the stress should not be assumed to remain constant in any cross-section, while the maximum value of this boundary stress is substantially higher than its corresponding theoretical

value. Other shapes of glue boundary may give even greater stress concentrations particularly if they include sharp re-entrant corners or cracks. As is well known in engineering design such sharp corners produce very high stress concentrations and are one of the main causes of failure both in statically but chiefly in repeatedly loaded structures. The stress developed at the free glue boundary needs a careful investigation. Some preliminary experiments as well as the research now in progress are given in Part II § 4-6.

§ 8. DOUBLE LAP JOINTS

The outer strips II and III (Fig. 45) of a symmetrical double lap joint cannot be subject to any bending as this would be of opposite direction

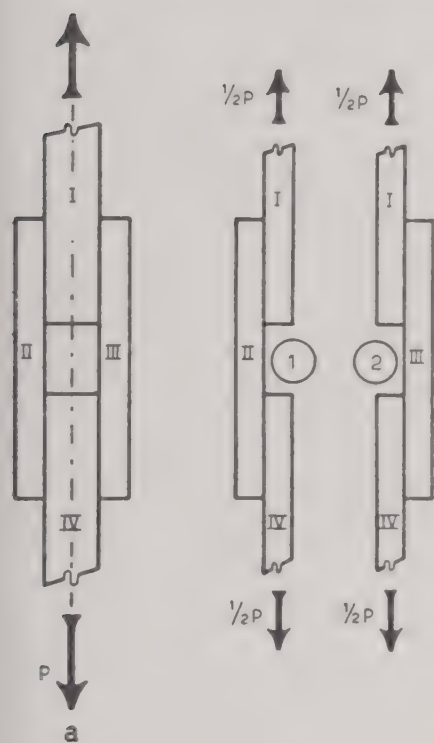
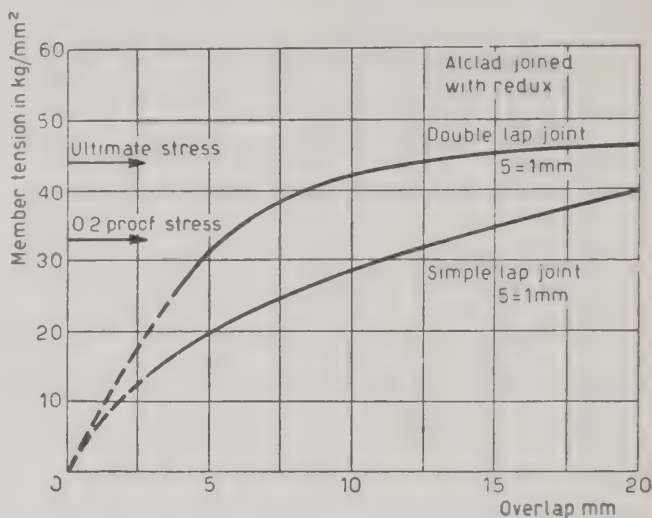


Fig. 45. The symmetrical double lap joint.

for each of them and would result in a change of the distance between them; such a change is prevented by the members I and IV which act as spacing blocks, at least when they are near enough to each other. Therefore assuming the members I and IV to be twice as thick as II or III and imagining the double joint to be divided into two equal parts (Fig. 45b) each composed of two simple lap joints in series, subjected to tension without bending, we can apply VOLKERSEN's theory which is based on such an assumption. According to the results of the comparison made in § 7 for $\Delta \gtrsim 4$, each of the two joint of Fig. 45b should be twice stronger than if the bending occurred while for $\Delta \gtrsim 0.3$ no appreciable difference should appear. This is supported by the results of tests of double lap joints¹⁶ which are illustrated in Fig. 46. The upper curve gives the stress at failure of either member of double lap joints of varying overlap, made of Alclad and joined with Redux, the members corresponding to I and IV of Fig. 45 being 2 mm thick, and III and IV being 1 mm thick. The lower curve gives the failing tensile stress of simple lap joints of the same overlap and 1 mm

thickness. The adhesive layer had a thickness of the order of 30 microns and therefore with G for Redux of the order of 100 000 p.s.i. and $E = 10\,000\,000$ it can be found that $\Delta = 4$ for $l \approx 8$ mm and $\Delta = 0.3$ for $l \approx 0.6$ mm. In accordance with the theoretical prediction the two curves do in fact coincide for $l \lesssim 1$ mm but quickly diverge for increasing overlap, reaching a maximum ratio of about 1.65 for $l \approx 6$, though for higher values of l they tend to converge again as the strength of the double joint is limited by the yielding in the Alclad sheets (See also § 9 on the effect of this yielding).



Courtesy of the Nat. Luchtvaartlaboratorium, Amsterdam

Fig. 46. Comparison between experimental curves for the strength of single and double lap joints.

If the members I and IV of thickness $2s$ were joined to each other by simple overlap of the same length l as before, for $\Delta \gtrsim 4$ and $k = 1$ the strength according to GOLAND and REISSNER would be (formula 16):

$$P_1 = l \cdot \tau_{\max}/n_{GR} = l \tau_{\max}/\sqrt{2 Gl^2/2 E s d} = \tau_{\max}/\sqrt{G/E s d}$$

while for the double joint it is (formulae 15):

$$P_2 = 2 l \tau_{\max}/n_V = 2 l \tau_{\max}/\sqrt{\frac{1}{2} Gl^2/E s d} = 2 \sqrt{2} \tau_{\max}/\sqrt{G/E s d}$$

or 2.8 times higher. It is obvious that symmetrical double joints are preferable to single lap joints of the same overall dimensions.

§ 9. GAP JOINTS

Usually the gap between the adherends is too small in comparison with their thickness and is overlooked in the calculation of the bending due to the eccentricity of the loading. In such cases the previous formulae will have a direct application, though it should be kept in mind that unless the adhesive is of the gap-filling type it may have a strength dependent on the

width of the gap (Sec § 12 "Residual Stresses"). Occasionally the gap is wide compared with the thickness of the adherends and then the eccentricity of the loading and the resulting tearing stress increase substantially. Such gap joints made out of three-ply board as in Fig. 47 are used for the testing of plywood glues. In this case the eccentricity of the loading of the outer

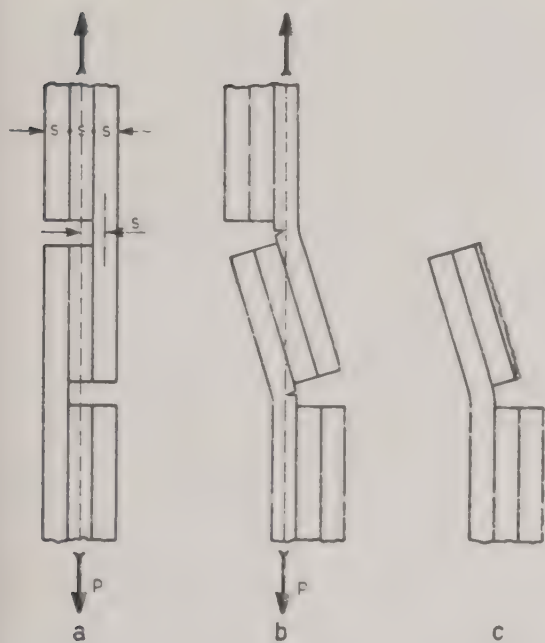


Fig. 47. Schematic explanation of the mechanism of failure of three-ply board test-specimens, which explains why these are half as strong as similar lap joints without the inserted third layer.

ply at the bottom of the grooves is s and the bending moment is Ps , twice as high as in the simple overlap (Fig. 38). This increase of bending moment can be expressed by a factor k equal to 2. Before any bending takes place the factor of shear stress concentration (formula 8) and the factor of tearing stress concentration (formula 11 or 12) for large Δ , will accordingly increase to about 1.75 times and 2 times their values for thin gap joints. The members are very stiff except at the bottom of the grooves which nevertheless are not wide enough to allow any appreciable bending in the elastic region: as a result no relief of stress by bending takes place as in Fig. 38. Furthermore the tensile strength of wood in a direction normal to

the grain is smaller than its strength in shear and therefore failure will depend on the tearing rather than on the shear stress. Thus the strength of these three-ply gap joints should be about half the strength of corresponding lap joints, a fact which is fully confirmed by test to destruction.

The highest stress appears at the bottom of the grooves of Fig. 47a at the corner nearest to the overlap, where the tensile stress due to the bending and the tearing stress will be increased by the sharp re-entrant corner. This can also be seen in the photoelastic stress patterns of similar joints shown in Part II § 4. As a result the failure starts at these places and spreads to the actual joint, as can be deduced from the deformation shown in Fig. 47b which precedes failure, and by failure itself which always occurs

in one of the outer plies very near to their glued face, leaving a thin wood skin attached to the adhesive as in Fig. 47c.

According to this account of the mechanism of failure of three-ply joints, their strength should increase if beyond the joint the adherends were of the thickness of a single ply, thus easily deforming and allowing a reduction of the bending moment.

§ 10. INFLUENCE OF THE MECHANICAL PROPERTIES OF ADHERENDS AND ADHESIVE

The theoretical investigation of the stress distribution in joints assumes that both adherends and adhesive are isotropic and obey HOOKE's law of elasticity. The main difference occurs with wood which, though obeying the law of proportionality even up to breaking point in tension, if well seasoned and rapidly loaded, yet is anisotropic and its mechanical properties vary with the direction relative to the grain and with the way of loading; it also shows plastic flow under sustained long-period loading. The anisotropy of wood has been the subject of special study and for its expression a number of independent primary constants have been assumed in place of the two — *i.e.*, E and m or G — needed for isotropic materials¹⁷⁻¹⁹. Thus as regards wood-to-wood joints the theoretical as well as the experimental results found with the help of isotropic models can only serve as indications of the expected absolute strength. Yet for the relative comparison between similar joints the theoretical results are sufficient, since the nature and the directions of the developing stresses do not vary considerably from joint to joint. But even metallic adherends do not always behave elastically, in particular with the modern glues with which the yield point of the metal is reached before the glue fails. The yield in the members will greatly increase the differential strain at each end of the overlap and will precipitate the failure²⁰.

In contrast to the yield of the adherends, any plastic flow of the adhesive has a relieving effect on the peak stresses of lap joints, since the yield will reduce the stiffness of the adhesive, thus reducing the factor Δ . But the effect is even stronger because with adhesives having a yield stress the highly stressed ends give way partially and thus redistribute the load more evenly throughout the joint. The effect is exactly the same as with the yield of the highly stressed end rivets of riveted connections which results in a more or less even distribution of the load between the rivets. A similar explanation accounts for the paradox sometimes observed when the growth

of strength of wooden lap joints is observed over a period of time; the breaking load is at first low due to lack of strength in the glue; as setting of the glue takes place the breaking load rises. Curiously enough, however, it then passes through a maximum (at which failure in the glue layer still occurs) and subsequently drops to a value at which, and after which, wood failure invariably takes place. At the peak value the joints break in the glue layer and at the same time are apparently stronger than the wood. At this peak value the glue is not fully hardened and because of its plasticity the load is distributed more evenly over the surface of the wood; later the glue becomes more brittle and the stress rises locally at the ends of the joints to a value which cannot be withstood by the wood.

For butt joints under tension the plastic flow in the adhesive is disadvantageous unless it is accompanied by work hardening. Consider for example a tensile joint consisting of two parallel rigid discs of radius R joined by a thin layer of a plastic adhesive of thickness d which behaves elastically up to its yield stress τ_y in shear, while at this stress it is perfectly plastic, *i.e.*, elongates without any increase of stress. The stress concentration which was found (see § 3) along the edge of the glue of butt joints will again develop as long as the stress is everywhere lower than τ_y , but as the load increases this limit will be reached and the overstrained material at the edge will flow under constant stress, thus reducing the irregularities of stress distribution. If then the stress concentration at the edge can be neglected, this example, according to N. A. DE BRUYNE²¹, will be very similar to the parallel plate plastimeter examined by J. R. SCOTT²², with the only difference that the applied load is tensile instead of compressive. After the appropriate change of sign the mean tensile stress σ_n , *i.e.*, load divided by area of plates, which just causes plastic flow can be written in the form:

$$\sigma_n = \frac{2}{3} \tau_y R/d \quad (18)$$

As σ_n is inversely proportional to d it follows that the system of the plastimeter is stable because any higher pressure will compress the plates, diminish the gap d , and thus automatically increase the mean stress under which no yielding occurs; with the plastimeter a limiting gap d can be reached for any load. But under tensile load any yielding will increase the gap and lower the mean stress at which the yield starts: the system is unstable and σ_n is the mean failing stress. For butt joints with such a semi-plastic adhesive the strength will be inversely proportional to the thickness; if the thickness is small the strength may well exceed the tensile strength of the adhesive, but then of course the peak stress at the edges will be

the factor limiting the strength since no yield and stress redistribution takes place. Tensile tests on glued and soldered joints do in fact show an initial rapid fall of strength as the thickness of the adhesive of glued and soldered joints is increased²³⁻²⁷ (Fig. 48). The dependence of tensile strength on thickness is, however, complicated by other factors such as the development of residual strains which are stronger for thick adhesive layers (§ 14), the alloying of the solder with the adherends, the ever present stress-concentration at the edges, and also the mechanical behaviour of the adhesive which may vary from complete elasticity to fluidity.

In fact strong joints can be made with thin layers of pure liquids between optically flat plates wrung together²⁸. Thus, condensed water vapour gave joints with a tensile strength up to 87 p.s.i., turpentine 52, paraffin 62, olive oil 44. These liquids were assumed to be in the form of very small droplets in large numbers adhering to both plates. The surface tension along the

perimeters of all these droplets was calculated for paraffin to correspond to about 1.3 p.s.i., which was insufficient to explain the high strength observed. On the contrary the existence of droplets diminished the working cross-section and the true stresses were estimated to be 871 p.s.i. for water, 514 for turpentine and 614 for paraffin. Such strengths should be expected: according to STEFAN's formula (See Chapter 3: The Rheology of Adhesives, p. 33) the product of the mean tension σ'_m by the time t of pulling apart is:

$$\sigma'_m t = \frac{3}{2} \nu R^2 / d^2 \quad (19)$$

Thus this product is proportional to the viscosity ν of the liquid adherend, to the square of the radius R of the areas in contact and inversely propor-

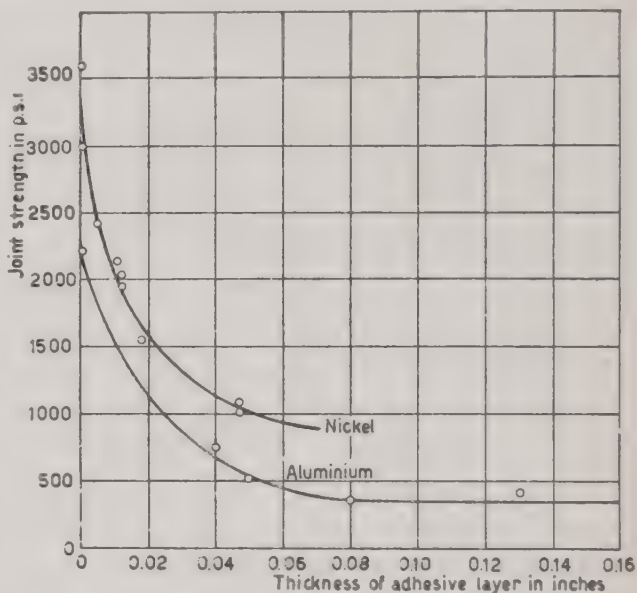


Fig. 48. Dependence of the strength of butt joints from the thickness of the adhesive layer. The upper curve gives the strengths of joints between nickel adherents, the lower curve those between aluminium adherents. The adhesive is a shellac composition.

tional to the thickness d of the liquid layer. Of course no such joint will be stable since even a small stress will cause the failure if it is applied for a sufficiently long period. Yet if the time needed for rupture is very long, the joint could be regarded as stable. Comparison of joint strengths should be done with due consideration of the breaking time.

However it should be pointed out that STEFAN's formula is founded on the assumption that the liquid flows between the plates when these are pulled apart, in other words that the liquid gives way in shear. Yet when d or t are very small the tensile stress σ_n predicted by formula (19) may reach a value which cannot be withstood by the liquid: failure will occur in tension and this formula will be valid no longer. The lack of proportionality between BUDGETT's results²⁸ and the viscosity of the liquids used may be attributed to the same cause. When pulled apart under usual conditions—for example, a drop between the thumb and fore-finger—liquids appear to have no tensile strength, but it will be noticed that the “failure” is a result of lateral flow of the liquid resulting in considerable lateral contraction or “necking” due to the absence of shear strength. The true tensile strength of a liquid can be found when lateral contraction is prevented. Thus water was subjected to a tension of 350 atmospheres²⁹ and ethylether to a tension of 70 atmospheres³⁰. The ultimate tensile strength of liquids can be calculated by the theory of nucleation from the energy required for the formation of a failure-initiating bubble³¹. The corresponding tension is very high; at room temperature it is 1320 kg/cm² for water, 138 kg/cm² for ethyl ether and 22 300 kg/cm² for mercury. The strength is found to be almost independent of the time of application of the tension and proportional to the power $\frac{3}{2}$ of the surface tension for the liquid in contact with its vapour.

But liquids are not the only adhesives to give butt joints with strengths considerably higher than their “apparent” strength, provided the gap is small enough. For instance, KONSTANTINOVA²⁶ found the strength of thin layers of solid paraffin between parallel plates to be higher than—about double—the tensile strength of paraffin. The explanation should be sought in the mechanism of the failure in the joint as compared with the actual tensile strength test. For example, when testing a rod of mild steel in tension we speak of tensile stress though the material fails in shear, as is shown by the LUEDER's lines and the cone of fracture which are at 45° to the direction of pull. The same can be said of all plastic and ductile materials: even when tested in tension they fail or start failing in shear because their resistance in shear is smaller than in tension. But in the thin layer between the two flats, the adhesive is constrained from deforming in shear

and more or less purely tensile stresses develop to which it can resist more than to shear, hence the higher strength obtained when the gap is narrow enough to guarantee this constraint. This is also clearly shown by experiments by OROWAN, NYE, and CAIRNS³², executed in 1945 and recently published in a review on the fracture and strength of solids by E. OROWAN³³, in which a joint made of a thin disc of tin, 0.4 mm thick and $\frac{1}{2}$ in. in diameter, welded by pouring molten tin between the flat ends of mild steel rods failed at a means stress of about 1250 kg/cm², while the strength of cast tin was 225 kg/cm² and even after correction to the "true" strength in notched bar tensile tests could not have exceeded 400 kg/cm². The transition from ductile failure at the circumference of the neck of a tensile specimen or at the edge of the notch of a notched specimen to brittle failure at the interior is also a proof of the above theory. The experiments with thin layers between parallel flat plates could be very useful as true tests of the tensile (brittle) strength of ductile materials if the strength of the adhesive could be dissociated from the strength of the adhesion.

All the previous discussions refer to the strength of the adhesive, though the joint may fail in the adherend, but this is outside the field of a study of adhesives, while as mentioned before, failures due to poor adhesion are rare with the modern adhesives, especially with the metal-to-metal ones.

The factor of time introduced in this discussion is fundamental. The striking dependence of the strength on the time of loading, found with thin liquid adhesives subjected to tension, is an extreme of the variations which happen in normal cases with butt as well as lap joints. All adhesives are plastic or semi-plastic in the meaning that under prolonged loading they will show some amount of creep, and therefore the length of loading which may allow the yield to take place or which brings failure before the yield occurs, will determine whether the adhesive will behave as ductile or brittle, *i.e.*, break in shear or in tension. Owing to the considerable effect of the time-factor on the strength of joints, a constant speed of loading is necessary in order to make any comparison possible, and such a speed is fixed by the corresponding test specifications.

The speed of application of the load will have a different effect on the various adhesives and adherends. A base of comparison is offered by the concept of the MAXWELL relaxation time and from that point of view similarity will exist for equal ratios t/λ where t is the breaking time and λ the relaxation time.

In a recent paper MCFARLANE and TABOR³⁴ study the adhesion between solid surfaces under various conditions. The presence of a thin liquid film between the surfaces is found to result in considerable adhesion affected

by its surface tension and viscosity. The formation of junctions between clean metallic surfaces, *i.e.* of the cold- or pressure-welding, is also studied.

§ 11. OTHER THEORIES

DE BRUYNE's theory of the strength of butt joints (page 111), together with the strength exhibited by liquid adhesives and with the change in the mechanism of failure from shear to tension, can give an explanation of the inverse relation between strength and thickness of adhesive without reference to other theories which are either uncertain or only partially valid. Thus the attribution of the high strength of thin joints to long range molecular forces by MCBAIN and LEE²³ is not acceptable in the light of present day knowledge. BIKERMAN²⁴ attributed the decrease of strength with increasing adhesive thickness to the higher probability of occurrence of a flaw where the failure would originate. However this theory accounts for two thirds of the difference and is valid only for brittle materials and certainly not for liquids, while plastic materials besides being mostly homogeneous, by their plasticity nullify the stress-concentration arising from any flaw.

§ 12. RESIDUAL STRESSES

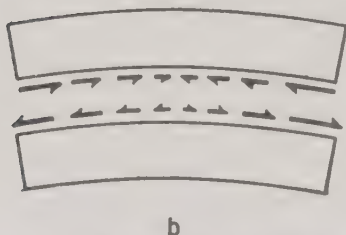
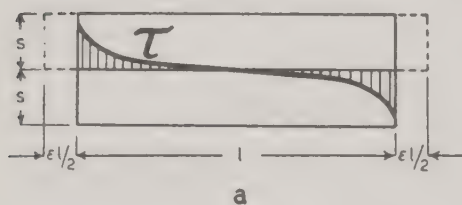
The greater number of flaws in thick layers of brittle adhesives is presumably due to higher strains and cracks resulting from the contraction of the adhesive in bulk. Occasionally these stresses may be high enough to cause spontaneous destruction of the joint. The existence of such stresses was ascertained by MYLONAS¹⁵⁻⁶⁶ with the photoelastic pattern obtained from slices of gap joints made with transparent glue (Part II § 5), though this pattern cannot be used for the quantitative determination of the residual stresses because the stiffness and stress-optical sensitivity of the glue vary throughout the process of setting.

The cracking due to the contraction of a material in bulk is also encountered in the setting of cement and the remedy is to mix sand which acting only mechanically brings an even distribution of the strains and avoids the formation of cracks. A similar method is the use of a filler in the glue, and experiments with wooden lap joints with a gap of one, two, and three millimetres filled with pure "Melocol H" glue³⁵, showed a drop of some 70% in strength from thinnest to thickest; whereas when 100% weight of inert filler was added to the glue, the strength was constant at all gap sizes and also was considerably higher than when pure glue was used. It should be noted that the pure glue joints failed in the glue while those with the filler failed in the wood, which

explains the uniformity of strength irrespectively of gap size. Photomicrographs of these gap joints showed that the pure glue layer was uneven and cracked while the one with filler was uniform without any cracking.

Another cause of residual stress is the differential thermal contraction of adherends and adhesive. The differential contraction is the main cause of failure of glass-to-metal seals and will be separately reviewed in § 14. Most of the modern adhesives and in particular those used for metal-to-metal bonding set at about 100° to 200° C above room temperature and considerable stresses may develop during cooling specially when the adhesive is brittle. The adjustment between the coefficients of thermal expansion of adherends and adhesive by the admixture of a suitable filler in the adhesive was found by TURNER³⁶ and MEISSNER and MERRILL³⁷ to increase the strength of butt joints, though it should be borne in mind that independently of its effect on the coefficient of thermal expansion the filler also produced an even distribution of the strains due to setting as well as to cooling and this action may have been the more effective of the two.

Residual stresses develop also by the shrinkage or swelling of the adherends owing to changes in their moisture content, as is discussed in the next paragraph.



From Distz, Grinsfelder and Reissner³⁸

Fig. 49. The shear stress distribution across the width of a double laminated beam of which the upper laminate expands uniformly by absorbing moisture.

the setting of the adhesive or even after a strong initial bond has been obtained.

In practice it has been found that wood members thicker than $1/8$ th in. present more difficulties in gluing than thin ones. It has also been observed that the delamination is stronger during drying and the subsequent shrinkage

§ 13. STRESSES IN LAMINATED WOOD

Every change in the moisture content of wood is accompanied by a change of volume (varying with species) in radial and tangential directions to the grain and therefore any non-uniform change of moisture content in a laminated wood structure may give rise to considerable internal stresses and may result in the destruction or delamination of the structure. The delamination may occur during the changes of humidity which accompany

of the laminates rather than during the swelling which accompanies an increase in humidity.

Two simple limiting cases of laminated structures have been investigated mathematically by DIETZ, GRINSFELDER and REISSNER³⁸ by minimum strain energy methods on the assumption of a plane state of stress. In the first case a two-layer laminated beam is examined when the one laminate expands in width owing to a change in moisture content. Had it been free this laminate would have expanded by $\epsilon_h l$, where l is the original width and ϵ_h the unit strain equal to αm , α being the coefficient of moisture expansion. A shear stress distribution similar to the one shown in Fig. 49a develops along the glue line owing to the restraint exercised by the other laminate. These stresses act in opposite directions on the glued sides of the two laminates and curve them as in Fig. 49b. The highest stress is found at the edges and is given by:

$$\tau_{\max} = 0.7 \epsilon_h \sqrt{E_x G_{xy}} \tag{20}$$

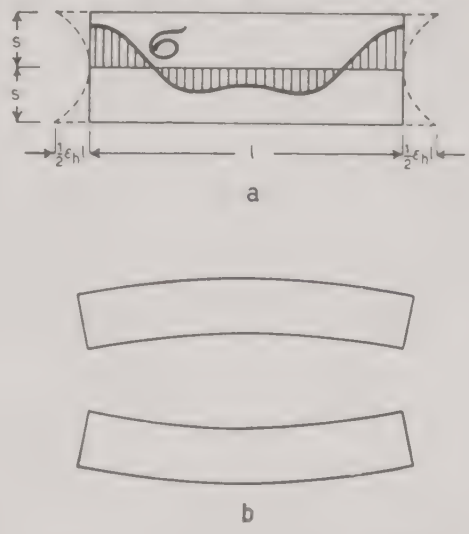
where E_x is the YOUNG'S modulus of the timber in the direction of the beam's width and G_{xy} the shear modulus between the directions of width and thickness.

A two-layer beam with a moisture content varying parabolically with the depth is next examined (Fig. 50a). Such a condition arises when a dry beam is suddenly brought in wet surroundings or a wet one in dry surroundings and before the moisture equilibrium throughout the beam is reached. If free to deform, each laminate would assume the curved shape of Fig. 50b where the fibres distant by y from the glue line would tend to expand by:

$$\epsilon_y = \epsilon_h \cdot y^2/s^2$$

The glue layer exerts only normal stresses on the glued faces which keep the laminates flat. The peak stresses are found again at the edges:

$$\sigma_{\max} = -0.45 \epsilon_h \sqrt{E_x} \sqrt{2E_y G_x} \tag{21}$$



From Dietz, Grinsfelder and Reissner³⁸

Fig. 50. The tensile stress distribution across the width of a double laminated beam of which either laminate curves inwards as a result of a parabolic distribution of absorbed moisture.

where E_x and E_y are the YOUNG's moduli of the timber in the directions x of the width and y of the thickness of the laminates and G_{xy} the shear modulus between these directions. The highest stress is a compression for an outward increasing humidity and tension for outward decreasing humidity.

According to these formulae the stresses developed in two-layer beams of various timbers and for a maximum change of moisture content of 16%, are given in Table 11.

TABLE 11
STRESSES DEVELOPING IN TWO-LAYER BEAMS OF VARIOUS TIMBERS
Max. change of moisture content: 16 %

	Shear stress		Normal stress	
	max. p.s.i.		max. p.s.i.	
	Edge-grain	Flat-grain	Edge-grain	Flat-grain
Ash	1 850	2 160	1 740	3 020
Douglas fir	660	880	940	1 580
Mahogany	1 060	1 150	910	1 720
Oak	1 660	2 020	1 360	3 240
Spruce	420	550	550	1 130
Walnut	1 590	1 590	1 330	2 130

Hard timbers having high elastic moduli develop higher stresses than soft timbers, while flat-grain laminations give rise to higher stresses than edge-grain ones. This is due to the considerably higher coefficient of moisture expansion in the tangential as compared with the radial directions, the difference being partly only compensated by the opposite differences of the YOUNG's moduli in these directions. The stresses given above are found theoretically and should serve only as an indication of the relative stress intensities to be expected in various conditions of lamination; other factors such as the plastic flow of wood and the yield of the adhesive doubtless reduce the peak stresses.

Though showing that peak stresses develop at the edges of the laminations and are responsible for any delamination occurring, yet the above paper does not explain the reasons for the easier delamination of thick laminates (formulae do not contain the thickness s of the laminates), which is attributed to the lack of intimate contact between thick laminates due to imperfect surfacing and rigidity. It also offers no explanation for the stronger delamination during loss as compared with an equal gain in moisture, as has been observed in practice. This is tentatively explained by

the plastic flow of wood which is more pronounced at high moisture contents and which relieves the peak stresses. The present authors consider that this may be one reason for such delamination, but that another cause is probably due to the sign of the peak stresses in each case. Thus according to (21) a gain in moisture ($m > 0$) gives rise to compressive peak stresses while a loss ($m < 0$) produces tensile stresses, in which the glue and the timber across the grain are weaker.

Formulae explaining the behaviour of thick laminates can be obtained by assuming that the adhesive layer deforms elastically both in shear and under normal stresses and that the laminates obey the laws of bending of rectangular beams *. These assumptions are valid when the flexibility of the adhesive layer is considerably higher than that of the laminates, as for example in the case of metal sheets glued together with a thick adhesive layer, yet they are included in this paragraph because they show the dependence of the peak stresses on the thickness of the laminates.

When the top laminate of a double beam suffers a loss m in moisture content, the resulting shear distribution in the adhesive layer will be similar to the one shown in Fig. 49, the peak shear stresses at each end being:

$$\tau_{\max} = 0.35 \varepsilon_h E \sqrt{Gs/Ed} \quad (22)$$

where G is the shear modulus of the adhesive layer and d its thickness, E is the YOUNG's modulus of either laminate and s its thickness, and ε_h is the unit contraction of the drying laminate which would have taken place if no constraint had been exercised by the other laminate. If α is the coefficient of moisture expansion:

$$\varepsilon_h = \alpha \cdot m$$

In the case of the double beam with a symmetrical parabolic moisture change of difference m , the developing stresses are normal to the interface and have a distribution similar to the one shown in Fig. 50. The peak stress at the edge is:

$$\sigma_{\max} \simeq -0.25 \varepsilon_h E \sqrt{E_a s/Ed} \quad (23)$$

where again $\varepsilon_h = \alpha m$ while E_a is the YOUNG's modulus of the adhesive. The peak stress is a tension for loss of humidity and a compression for an increase.

It may be noted that the product $\varepsilon_h E$ represents the stress σ which would prevent the laminate from changing its unit length by ε_h , so that the peak shear and normal stresses are given as functions of σ .

The analysis of a single laminate bonded to a rigid base is more complicated (Fig. 51). Both shear and normal stresses develop when the laminate

* Unpublished report by C. MYLONAS.

changes its moisture content by m , which correspond to a strain ε_h . Their distribution is as in Fig. 51 b and c, the maxima being:

$$\tau_{\max} = \varepsilon_h G \frac{l}{s} \Psi_1(\delta, l/s) \quad (24)$$

$$\sigma_{\max} = -\varepsilon_h E \Psi_2(\delta, l/s) \quad (25)$$

$$\text{where } \delta = Gs/Ed$$

and Ψ_1, Ψ_2 , are exponential functions only of δ and l/s , increasing with s .

Thus all formulae contain the term s and the peak stresses expressed by them increase with the thickness of the laminates, as has been practically experienced. According to formulae (22) to (25) the stresses can be diminished by using thinner or softer laminates as well as thicker and more flexible adhesive layers.

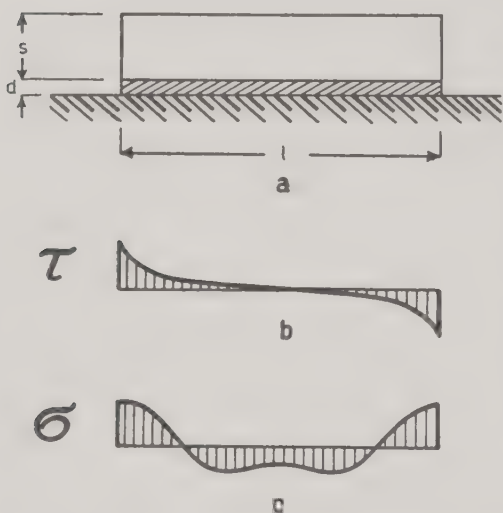


Fig. 51. Shear and tensile stress distributions across the width of a laminate bonded to a rigid base through an elastic adhesive, caused by a uniform change of width.

A theoretical investigation of the stress distribution in a rectangular block solidly adhering to an undeformable solid and contracting owing to a temperature change has been made by B. J. ALECK³⁹. The mathematical treatment is of the same nature as GOLAND and REISSNER'S¹⁰: the stress normal to the interface is arbitrarily assumed to be:

$$\sigma_x = f_1(x) + y f_2(x) + y^2 f_3(x)$$

and with the help of the differential equations of equilibrium and of the boundary conditions the normal stress σ_y parallel to the interface as well as the shear stress τ_{xy} are expressed in terms of y and derivatives of f_i . The principle of minimum strain energy leads then to six simultaneous differential equations. The solution is given in form of series which are solved numerically for a ratio of length l to thickness s of glued block longer than five. Calling ε the unit thermal contraction and E the YOUNG'S modulus of the block, the ratio $\sigma_y/E\varepsilon$ is found higher at the edge of the adhering side where it has a value 10.2; it drops to almost zero within a distance $x = 0.1s$ from the free edge, thus suggesting that the accurate solution might give a concentrated load. The ratio $\sigma_x/E\varepsilon$ is nil at this same edge, increases to -2.0 within a distance $x \approx 0.25s$ and then tends to a constant

value of -1 for $x \geq 0.8 s$. The ratio $\tau_{xy}/E\varepsilon$ also starts from zero, increases to 2.7 for $x \leq 0.08s$ and for $x \geq 0.4s$ drops to almost zero. It is thus seen that the highest stress develops at the edge of the glued face and is a tension for a contracting block and a compression for an expanding block. As has been already mentioned this explains the cause of the easier delamination accompanying a loss (contraction) rather than a gain (swelling) of humidity of glued wooden laminates.

§ 14. GLASS-TO-METAL SEALS

In sealing glass to metal the problem is not to make a joint capable of withstanding large external loads but to avoid the development of residual stresses sufficiently large to cause spontaneous disruption. The subject of glass-to-metal seals is extremely wide because of its importance for the electric and electronic industries, and the present short paragraph deals only with the causes of development of stress, with some methods for reducing it and, also with some calculations of stresses to be expected in certain

types of seals. Information about sealing metals and glasses, the nature of their adhesion, and the various methods of sealing should be obtained from the various relevant papers or from monographs such as the recently published thorough study *Glas-to-Metal Seals* by J. H. PARTRIDGE ⁴⁰.

No internal stresses would develop if the coefficients of thermal expansion of glass and metal

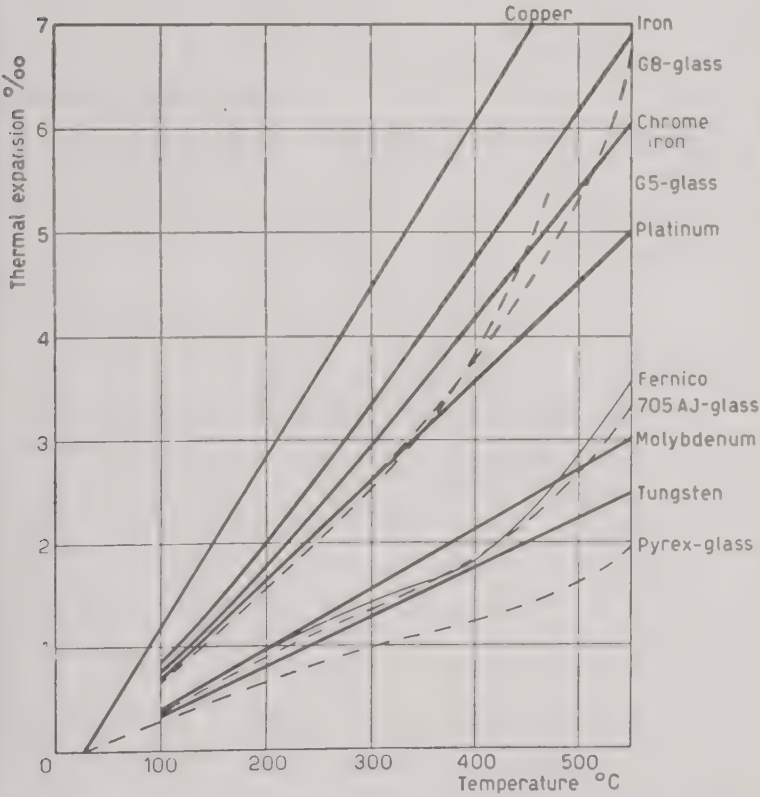
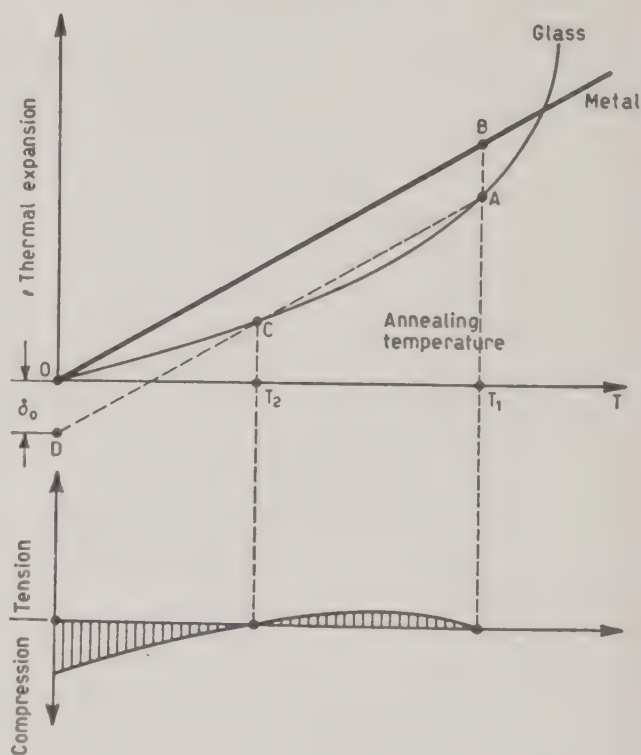


Fig. 52. Thermal expansion of various glasses, metals and sealing alloys.

were exactly the same within the whole range of temperature used. Such a perfect 'matching' of the seal constituents is never possible, mainly because of the transition point in the coefficient of thermal expansion of all glasses, a change which with few exceptions (*i.e.*, Fernico and Fernichrome alloys) is not found in any metal or alloy in the range of temperatures up to the softening point of glass. Fig. 52 shows the total unit thermal expansion of various metals and alloys and of several sealing glasses⁴¹. All metals and alloys have practically straight line characteristics while the curves of all glasses, though being more or less straight at first, have a transition point below their softening temperature, above which the rate of expansion rapidly increases. A difference in size would appear in the components of the seal if they could freely contract; this is prevented by the adherence between them which gives rise to a stress of opposite direction in each of them, of magnitude such as is necessary to produce strains which added to the thermal strains will make the total contractions equal. Therefore the internal stresses are proportional to the total differential thermal strain of glass and metal. Accordingly a stress-free condition at room temperature is not necessarily the result of an absolute coincidence of the expansion curves of glass and metal, but can also be achieved when their total contractions from the sealing or annealing temperatures are equal, though at intermediate temperatures this condition may be unfulfilled and stresses may exist.



From Radston and Stanworth⁴¹

Fig. 53. The development of stress during cooling from the annealing temperature of a glass-to-metal seal.

But the total contractions of the two constituents of a seal are equal when their expansion curves, coinciding necessarily at room temperature,

intersect again at the annealing temperature from which the seal is cooled. The second intersection is possible because of the upward turn of the glass expansion curve (Fig. 53) so that stress-free seals can be produced by matching glasses with metals of equal total expansion at the annealing temperature only. A perfect matching of this sort is seldom possible and usually unnecessary because glass can withstand stresses of a limited magnitude. The safe limit in tension ⁴¹ is around 1 kg/mm² (1400 p.s.i.) while in compression it can be considerably higher, so that the usual tendency is to produce seals with initial compressive stresses in the glass. Thus for example the expansion curves of a sealing glass and metal before sealing are diagrammatically shown ⁴² in Fig. 53. At the annealing temperature T_1 the glass has expanded less than the metal, yet upon cooling they must retain equal lengths. The difference AB can be imagined to be compensated by a mechanical differential strain $\delta_0 = BA$ imposed partly on each constituent. As the internal stresses depend on the total difference in contraction and not on the absolute contraction of the constituents it may be supposed that all the strain BA is produced in the metal and superimposed on the thermal strain T_1B leaving a total strain T_1A for the metal as well as the glass at the annealing temperatures. If free to contract and gradually cooled to room temperature, the metal, loaded always with the stress which produces the strain δ_0 , would contract along the straight line ACD distant from BO by δ_0 , while the glass would follow the same curve ABO. Their differences at any temperature plotted from a horizontal axis are a measure of the stress which develops when glass and metal are not free to contract but adhere firmly to each other. The lower diagram of Fig. 53 shows the corresponding variation of the internal stress σ of the cooling seal. Tensile stress will at first gradually build up, reach a maximum and then decrease to zero at a temperature T_2 , then reverse sign and become compressive of increasing magnitude down to room temperature. Such a variation of stress is easily ascertained by photoelastic measurements. With the Fe, Ni, Co and Fe, Ni, Cr alloys Fernico and Fernichrome, which have a transition in their thermal expansion almost identical with that of a hard glass, the differential contraction can be practically nullified (see, for example, in Fig. 52 the coincidence of the expansion curves of Fernico and glass 705 A).

Special alloys matching the expansivity of hard glasses have been studied by H. SCORR ⁴³. They are nickel-steel alloys containing cobalt, such as the alloy kovar which can be readily sealed into Nonex glass.

It has been tacitly assumed that the annealing or softening temperature of glass is sharply defined and that below it the glass behaves as a solid,

whereas glass softens gradually throughout a range of temperatures and by definition ⁴¹ the annealing range is contained within the temperatures at which glass loses 9/10ths of any internal stress in 15 minutes (upper limit) and 4 hours (lower limit). If kept within this range for a long enough period, the glass will lose all the stress already set up during the previous cooling and contraction from the sealing temperature. The stress-release will not take place when the rate of cooling through the annealing range is high because the viscosity of glass is still considerable. A lengthy anneal of glass at a fixed temperature followed by a relatively rapid subsequent cooling can alter the virtual temperature from which internal stress starts building-up as well as the resulting final stress at room temperature ⁴¹.

Other factors affecting the development of stresses in glass-to-metal seals are the change of the contraction of glass after prolonged heating at the lower annealing temperature ^{44, 41, 45} as well as the existence of some amount of viscous flow at temperatures below the annealing range which results in a dependence of the contraction curve on the cooling rate ⁴¹. Another potential factor is the yield of sealing metals such as copper, which though expanding considerably more than any standard glass, yet if of small diameter, do not give rise to dangerous stresses in the glass ^{41, 46}.

It has been observed that glass is weaker on its free surfaces because of the existence of microscopic flaws which initiate failure. As a consequence the strength of glass is increased by rapid cooling which solidifies the outer layers first so that harmless compressive stresses are developed in them during the subsequent contraction of the interior which, being stronger, resists the tension to which it is subjected. Any tension to which the glass

may be later subjected will be diminished by the amount needed to neutralize the already existing compressive superficial stress of the faces ⁴⁷. A similar distribution of stresses arises in seals made with glass having a lower coefficient of expansion than the metal wire ⁴⁸.

The magnitude of the stresses resulting from the causes already investigated will also depend on the relative size and the shape of the sealed parts. For example the radial and tangential stresses p_r and p_θ respectively, of a long glass cylinder sealed on to a concentric metal wire (Fig. 54) vary with the distance from

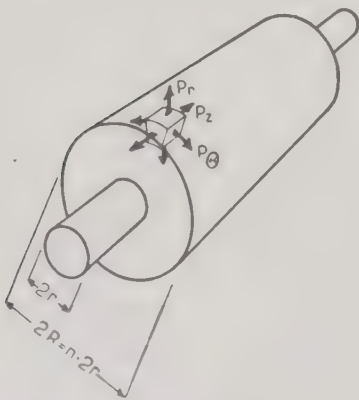


Fig. 54. Radial (p_r), tangential (p_θ), and longitudinal (p_z) stresses in a long glass cylinder sealed to a concentric metal rod (long bead seal).

the axis and are highest at the glass-to-metal interface, while the longitudinal stress p_z is constant throughout the thickness of the glass^{41, 42, 48, 49}. The highest values of these stresses depend on the relations between the elastic constants of the two materials and on the ratio n of their radii but are always proportional to the product $E_g \delta$ of the YOUNG's modulus of glass by the total differential contraction which is taken as positive when the wire contracts more than the glass. It is useful to consider this product as the stress which would develop in a glass rod tending to contract by δ and restrained from so doing by an absolutely rigid frame to which the rod ends firmly adhere. Thus the three stresses can be represented as multiples or fractions of this hypothetical stress $E_g \delta$.

For example the ratios for increasing values of $n = R/r$ have been

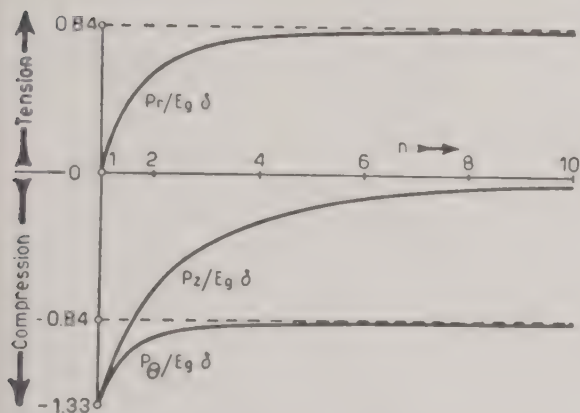


Fig. 55. Variation of the radial (p_r), tangential (p_z), and longitudinal (p_θ) stresses with the ratio n of the outer diameters of the glass cylinder and metal rod of figure 54.

($n \gtrsim 5$) it reaches the value 0.84 which for $E_g \delta = 670\,000 \text{ kg/m}^2$ and $\delta = 2 \cdot 10^{-4}$ would give a radial tension of some 110 kg/cm^2 or 1.1 kg/mm^2 which is considered a safe value⁴¹. When the glass contracts more than the metal, δ is negative and the sign of the stresses given in Fig. 55 is reversed: p_r is then compressive and p_z and p_θ tensile, the two last mentioned being the most dangerous stresses in the seal, p_θ as being the highest tension in the interior of the seal and p_z the highest tension at the surface.

The method of evaluation of the stresses due to PORITSKY⁴⁹ and HULL and BURGER⁴¹ has been extended by RAWSON⁵⁰ for similar cylindrical seals in which the metal component is not a solid rod but a tube. The radial, hoop, and axial stresses at the interface are given as functions of the

calculated for the particular case of glass to molybdenum seals where the YOUNG's moduli have a ratio $n = 0.186$ and POISSON's ratios are $m_g = 0.25$, $m_m = 0.17$. The results are shown in Fig. 55: the radial stress p_r is a tension, and the hoop and axial stresses p_θ and p_z are compressions when δ is positive, *i.e.*, when the metal contracts more than the glass. For this glass-metal combination p_r is most dangerous as being the only tensile stress; in thick glass seals

ratios of the three radii, namely the inner radius of the metal tube, the radius at the interface between metal and glass, and the outer radius of the glass. It is interesting to note that in seals of a thick glass tube on a thin-walled metal tube the stresses are low since, as should be expected, the tube is then weak and deforms under the pressure of the glass without producing a high stress in the glass. Thus it was found possible to seal thin-walled metal tubes through glass even though their expansion curves differed considerably.

The validity of the above theoretical calculations has been experimentally confirmed by photoelastic measurements⁴² on actual glass seals which closely coincide with the theoretical predictions. Nevertheless it is pertinent to remark that none of the investigators appear to have examined the possibility of any "frozen stress" developing in the glass during cooling, *i.e.*, of birefringence which would persist even after removal of the causes of the stresses, as for example by cutting the glass in pieces or better by dissolving the stress-producing metal in an acid. Such a property has been detected by FILON^{51, 52} in blocks of glass which had been cooled under considerable longitudinal pressure. The birefringence observed after the removal of the external pressure varied with the composition of the glass and could be interpreted as a tension or as a compression in the direction of the external loading. As these stresses were not in equilibrium throughout the block they could only be fictitious or "frozen stresses" similar to those which may be produced by the cooling under load of various plastics.⁵³

The calculated values of these stresses are only valid for long seals and at regions away from the ends. The ends themselves will produce a stress concentration which will depend on their shape. The general shape of the stress trajectories near the ends of some seals of usual shape given by MYLONAS are shown in Figs. 56 a–d. The stress trajectories are the same whether the glass or the metal contracts more but the tension and compression shown on them as well as on the boundaries correspond to a higher contraction of the metal; for a higher glass contraction the direction of the arrows should be reversed, and compression and tension interchanged. In (a) the most highly stressed area is at the corner near the edge of the interface, and it is a tension which makes the seal unsafe. The tapering shape (b) gives rise to a longitudinal compressive stress all along the boundary, the highest being at the tip according to the curve $p_z/E_g \delta$ of Fig. 55 which gives a maximum for $n = 1$. The only tensile stress which develops in the radial direction diminishes with the thickness and becomes zero at the tip, as shown by the curve $p_r/E_g \delta$ of Fig. 55. The shapes of Figs. 56 c and d achieve similar results to a minor degree; the tension on the face reverses sign through a point of zero stress in the plane of the

drawings and becomes compressive near the interface where the highest radial tension occurs. The diminishing thickness of glass near the tip reduces the highest radial tension.

The shape of the stress-trajectories in similar glass-to-metal seals have been sketched by W. J. SCOTT⁵⁴, but without sufficient detail.

Very interesting examples of the photoelastic investigation of the stress distribution in short flat two-wire seals are given by O. ADAMS⁵⁵ as well as in the recently published monograph of J. H. PARTRIDGE⁴⁰.

Adhesion of glass to metal can also be effected through an intermediate adhesive layer other than an oxide film, as for example with the thermo-setting synthetic adhesive known under the trade name of "Araldite"*^{56, 57}.

The curing temperature of this resin can be varied from 180° to 240° C. These temperatures are below the transition points in the expansion curves of any of the usual glasses or metals and therefore the differential contraction will be equal to the temperature drop from the hardening point to room temperature multiplied by the difference of the two constant coefficients of thermal expansion. The hardening point is not the curing temperature, as the glue is plastically deformable down to about 100A C and only below this temperature will internal stresses start to appear. However, high stresses can

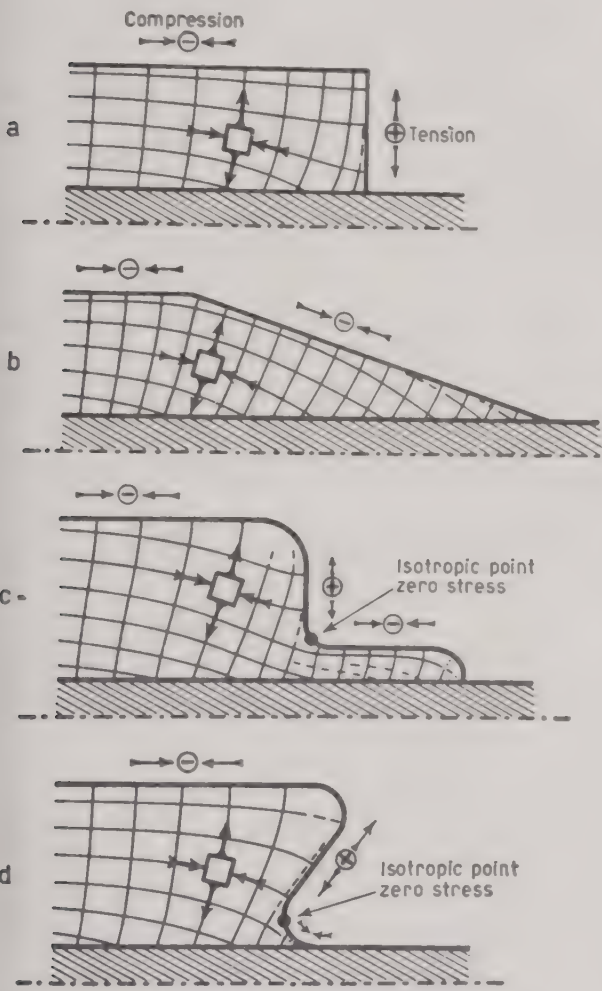


Fig. 56. Stress-trajectories in a section of symmetry of long glass-to-metal seals of usual shape. The isotropic points shown in (c) and (d) are stress-free points.

* A synthetic resin adhesive developed by Messrs. Ciba Ltd., Basle, and produced in England by Aero Research Ltd., Duxford, Cambridge.

develop even with such small temperature changes if the bonded materials are not suitably matched. Thus brass and glass cannot be glued together because of the considerably higher contraction of the metal: as shown in Fig. 57 the glass of a flat inspection window glued on to its brass ring by Araldite adhesive was split in its plane into two thinner discs. The brass ring had no rim protruding around the circumference of the glass plate; this was glued only on its flat face near its perimeter and the stress resulting from this differential contraction was transmitted to it by the adhesive alone.

The low temperatures needed for curing this adhesive allow steel to be matched with some hard glasses although the bond develops considerable stress. Better results are achieved by using special alloys (usually Ni-Fe)



Courtesy of Aero Research Ltd., Duxford Cambridge

Fig. 57. Cleavage fracture in its own plane of a circular glass inspection window bonded to its brass ring by Araldite adhesive. The differential contraction between brass and glass gave rise to a stress which produced failure in the glass.

of suitable coefficient of expansion. Thus for example in Fig. 58 is shown to the left a steel rod which broke off the glass to which it was bonded by Araldite (failure 100% in glass), whereas to the right is shown a sound bond between glass and a rod of Fernichrome alloy. Of course the strength of the seal will be independent of the coefficients of thermal contraction of the materials bonded together when the adhesive sets at room temperature, as for example does the cold-setting Araldite adhesive.

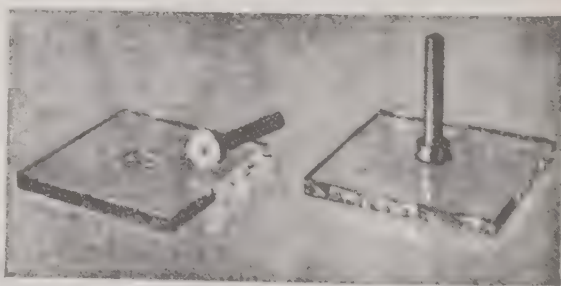


Fig. 58. (Left). Failure in the glass resulting from the differential contraction of a steel rod and the glass to which it was bonded with Araldite. (Right). Strong similar bond obtained with a rod of Fernichrome alloy which almost matches the expansion of glass.

Courtesy of Aero Research Ltd., Duxford Cambridge

PART II

EXPERIMENTAL INVESTIGATION
OF THE STRESSES IN JOINTS

§ 1. INTRODUCTION

As has been pointed out in Part I § 7 the theoretical analysis of the stresses in joints leads to some conclusions which are partially incompatible with actual conditions. Thus both VOLKERSEN as well as GOLAND and REISSNER assume that the stresses in lap joints are constant across the thickness of the adhesive layer and come to the conclusion that with flexible adhesive layers the highest shear develops at the edges of the overlap. The adhesive layer, however, has a finite thickness and ends in free glue-to-air surfaces at each end of the overlap. On such free boundaries the conditions of equilibrium limit the virtual stress to simple tangential tension or compression without any shear. A longitudinal shear stress component may exist only at places where the boundary forms an oblique angle to this direction. Thus the assumption of constant stress across the adhesive is not permissible and the conclusion that the highest shear stress develops at the edges of the overlap is not altogether correct. It is true that the highest relative displacement of the adherends occurs at the edges but the resulting stress distribution consists of stresses tangential to the boundary and with a magnitude depending on the shape of this boundary. For example a concave boundary will be in tension on the side of the protruding adherend on which the load is applied, and in compression on the side of the ending adherend, thus necessarily developing an intermediate stress-free point. With a square boundary the areas of high tension and compression will be confined to the two corners where the edge meets the adherends whereas the intermediate area will have an almost uniform stress produced by the tearing tendency of the joint.

A better knowledge of the stresses developing in joints and their dependence on the shape of the adhesive boundaries is obviously necessary and is acquired experimentally. The obvious check on the overall strength of a joint is the test to destruction but this gives no clue as to the specific cause of rupture or any indication of how to improve its strength. The necessary information can only be obtained from the knowledge of the stress distribution throughout the whole joint. It can be acquired experimentally by measuring the stresses actually developing in models similar to real joints and similarly loaded.

§ 2. THE PRINCIPLE OF SIMILARITY

Though the models used in the experiments may differ from the actual joints both in their dimensions and in the materials of which they are made, yet under certain circumstances model and actual joints are comparable and the stresses in the latter can be found from those of the former by a simple multiplication by a factor of proportionality or scale constant. Structures comparable in such a way are called *similar* and the study of the conditions under which the comparison is possible as well as the determination of the scale constants constitutes the *theory of similarity* of such structures.

The theory of elasticity shows that the stress distribution in plane, uniform structures, free of any holes with unbalanced forces, is independent of the elastic constants; the stress distribution in two structures will be proportional when these are geometrically similar and are loaded in a similar way. If F_c is the linear scale of the two structures and F_p the ratio of the applied forces, the scale F_σ of the stresses will be:

$$F_\sigma = \frac{F_p}{F_c^2}$$

The stress distribution of structures with unbalanced holes or of three-dimensional structures is again independent of the YOUNG's modulus E of the material but depends on POISSON's ratio m , though the changes resulting from a different value of m are very small and can usually be neglected^{52, 53}. Thus the stress-distribution in a steel or stone structure can be calculated from the corresponding distribution occurring in a similar structure made of glass or bakelite or even gelatine, provided all these materials behave elastically.

It is not always necessary to insist on absolute geometrical similarity: with joints^{15, 66} for example, the stress distribution can be expressed to some degree of accuracy by the ratios of the peak to the mean stress, or in other words, with the factor of stress concentration, which is the subject of main interest in all the investigations; two joints will be called similar when their factors of stress concentration are equal. But as calculated in Part I (see p. 97-104) the factors n of shear stress concentration and n_s of tearing stress concentration of joints with flexible adhesive layers are given by:

$$n = f(\Delta, k) \tag{7a}$$

$$n_s = k \sqrt{\Delta} \tag{12a}$$

where Δ and k have the values given by (2a) p. 97 and (4) p. 98. Thus finally the conditions of similarity are reduced to the equality of the coeffi-

cients Δ and k (as well as on the value of POISSON'S ratio m_a of the adhesive, since the simplified formula (12a) was obtained by assuming m_a constant and equal to 0.33): when this is fulfilled the joints should be comparable. Therefore it is permissible to experiment on models of joints made in a size and of materials facilitating the tests and draw conclusions on the behaviour of real joints having the same k and Δ . An indication of the validity of this theoretical criterion of similarity is provided by the various tests to failure of lap joints; their strengths are related to the "joint factor" ⁶ or to the factor Δ by the formulae of VOLKERSEN and PLANTEMA respectively (see Part I § 7). Therefore it can be assumed that the criterion of similarity is valid, although it would be desirable to have a more exact experimental verification.

The above conclusions are valid only when adherends and adhesive behave elastically: it should be noted that then similarity is independent of time. When yield occurs the time variable should also be considered, and will depend on the law of the yield. Unless the materials of the joints have proportional yield curves it is impossible to obtain similarity, since no fixed time-scale will exist between two models. One of the few instances susceptible of giving true similarity is when Newtonian liquids are used as adhesives between elastic solids, since obviously the time-scale will be proportional to the ratio of the viscosities. With actual adhesives a compromise may be reached by assuming that their rheological behaviour follows a concrete law from which the time scale may be derived; for example with materials following the MAXWELL relaxation law the ratio of the MAXWELL relaxation times will determine the time scale since only then will their respective stresses have the same ratio throughout the process of relaxation.

Such a simplification may lead to serious errors and in general similarity is only possible with one and the same yielding material, in which case the time scale is unity ⁵⁹, *i.e.*, the speed of loading should be identical, a precaution which is always imposed by the various testing specifications.

Usually it can be assumed that the governing factor in the strength of a joint is the stress distribution which develops in adherends and adhesive of perfect elasticity, by assuming that the yield, though modifying these stresses, yet usually affects them to a small extent and certainly in the same amount for any one material, the standard time of testing contributing considerably to this result. Thus the elastic stress distribution is sought and the highest elastic stress concentration is considered as a criterion of the strength of the structure.

In the experimental determination of the stress distribution it is essential

either to obtain absolute similarity by using the same materials or to seek the elastic stress distribution by using elastic materials. The phenol-formaldehyde resin Catalin 800 which is used in the photoelastic tests described later, yields considerably under constant load, but its stress strain-time relation was found by C. MYLONAS⁶⁰ to be of such a nature that no redistribution of stress occurs and the stress distribution is similar to that of a perfectly elastic body.

Another departure from true similarity takes place when the width of the model joints is small as compared to the thickness of the adhesive layer, as happens in most of the photoelastic tests of joints. In actual joints of large width the adhesive is in a state of plane strain over most of the width, a condition which is also postulated in the theory of GOLAND and REISSNER¹⁰. Yet when the width is small the adhesive can expand laterally more or less freely, and this results in a state of plane stress. In the theory of elasticity⁶¹ it is shown that the stresses in the two states are the same when the body consists of one material only and when the same external forces act on its boundary. As actual joints are made of two different materials bonded together, the states of plane stress and plain strain will give rise to different stresses. This difference has not been investigated yet. It is, nevertheless, clear that model joints with large width should be preferred to thin models.

§ 3. EXTENSOMETER TESTS ON LAP JOINTS

The shear stress developing at various points of the 3 in. long overlap of two $\frac{1}{4} \times \frac{1}{4}$ in. mild steel bars bonded by a "Redux" layer 0.025 ± 0.001 in. thick was estimated from the relative displacement of these bars measured by an optical lever*. The applied loads were very low so that HOOKE's law could be assumed to hold even in the region of high stress. The shear stress distribution is found to be as in Fig. 59a. The criteria of similarity are the factors Δ and k . With the value of $G = 280\,000$ p.s.i. estimated from the experimental data the factor Δ of the theory of VOLKERSEN is found by formula (2a):

$$\Delta = 13.5,$$

while $W = 2$, since the members of the joint are equal. The diagram of Fig. 39 gives a factor of stress-concentration:

$$n \approx 2.6$$

and since the mean shear is 302 p.s.i. the peak should be

$$\tau_{\max} \approx 2.6 \cdot 302 = 784 \text{ p.s.i.}$$

* Unpublished tests made by B. COOPER at the Cambridge University Engineering Laboratory.

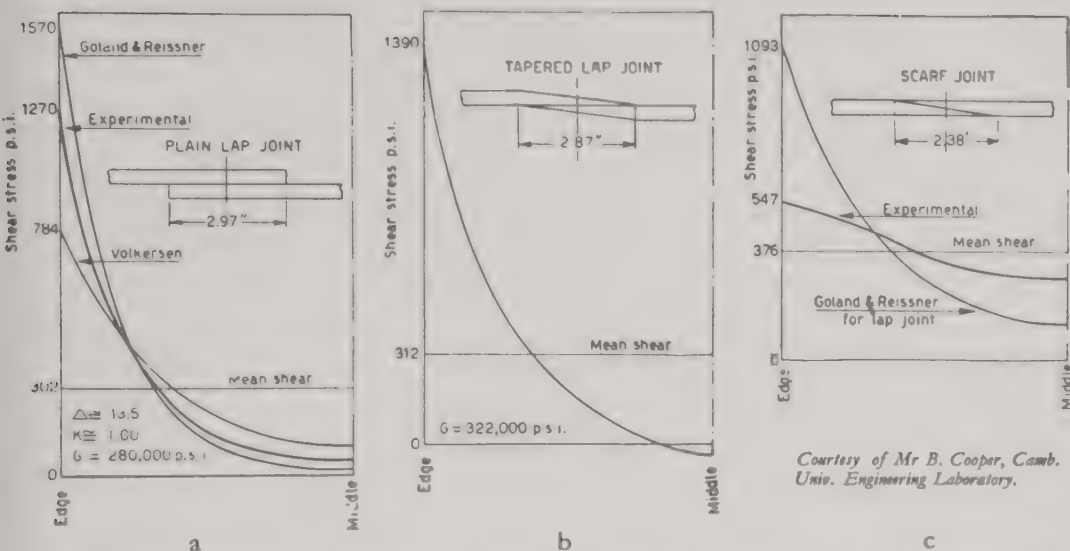


Fig. 59. Experimental determination of the relative displacement of the adherends of lap joints: (a) plain lap joint, (b) tapered lap joint, (c) scarf joint.

The calculation of the factor k of the theory of GOLAND and REISSNER will be given only as an example of the application of this method, because owing to the very short length of the members beyond the overlap, the flexibility of the joints is nil and k is virtually equal to unity*. If the members were considerably longer then the product $l/s\sqrt{p/E}$ (see p. 98) would be found equal to 0.13 ($l \approx 3.00$, $s = \frac{1}{4}$, $p = 3624$ psi. and $E = 3 \cdot 10^7$) which according to the graph of Fig. 40 corresponds to $k = 0.83$. For this value of k and for $\sqrt{2\Delta} = 5.2$, Fig. 43 gives by interpolation $n = 4.7$ and therefore τ_{\max} would be 1420 p.s.i. Nevertheless as already explained k is equal to unity and from the same Fig. 43 it may be found:

$$n = 5.2$$

according to which the peak stress according to GOLAND and REISSNER is:

$$\tau_{\max} = 302 \cdot 5.2 \approx 1570 \text{ p.s.i.}$$

The full curves of stress distribution found by both theories are included in Fig. 59a for comparison. As should be expected, the experimental results are in better agreement with the theory of GOLAND and REISSNER than with the theory of VOLKERSEN.

Similar tests were made on a tapering lap joint (Fig. 59b) and on a scarfed joint (Fig. 59c). Both gave stress concentrations smaller than the plain

* See footnote on page 132.

lap joint, though the scarfed joint much more so. The factor n in the three tests was respectively 4.52, 4.46 and 1.45. All these tests were made with very light loads and the stress distribution observed would be modified at higher loads because of the resulting creep and of the bending of the adherends (see Part I § 4). It should be pointed out that the above tests are a good check on the theories of VOLKERSEN and of GOLAND and REISSNER because they follow the same procedure, namely they all find the relative displacements of the adherends, and from them calculate the shear stresses by assuming that they are constant within any cross-section of the adhesive. For the same reason these experiments do not enlighten us as to the exact nature and magnitude of the stresses developing, which as was explained in Part I § 7 and Part II § 1, vary across the thickness of the adhesive and should be purely tensile or compressive at the edges of the overlap.

§ 4. PREVIOUS PHOTOELASTIC TESTS

The stress distribution in a rectangular block subjected to shear on two opposite faces as well as in a double shear block very similar to a double lap joint were investigated by COKER^{62, 52} and calculated theoretically by INGLIS^{63, 52}. The conditions of loading were similar to those of joints with stiff non-deforming adherends and thick and flexible adhesive but without tearing stresses since the symmetry of the double shearing prevented the bending which develops in single lap joints. These investigations were only concerned with the stress distribution along the plane of symmetry parallel to the sheared faces of the block although by far the highest stresses developed at the corners. At each end of this plane the stress was zero, in agreement with the opinions expressed in Part I § 7 and Part II § 1. The shear increased to a maximum within a short distance from the free edge and then diminished slightly to a practically constant value over the central area. For short blocks the shear stress had a single maximum at the middle of the length.

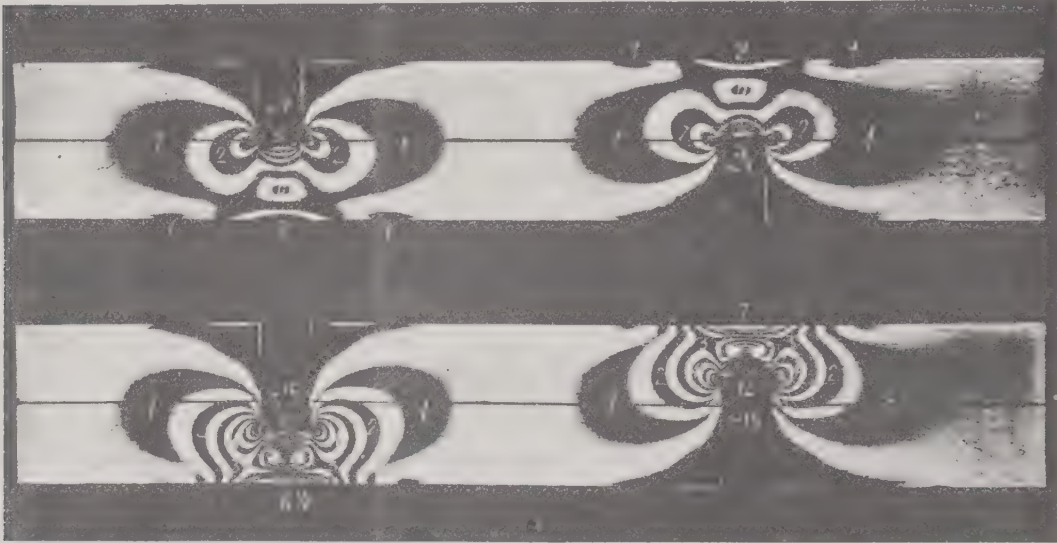
The stress distribution in two members bonded together by a uniform layer has been investigated as a means of determining the strength of spot-welds⁶⁴. The specimens, which could be also considered as models of joints, were machined out of a plate of "Trolon" (phenol-formaldehyde resin) 10 mm thick and consisted of a continuous piece of material; the adherends were 10 mm thick and 0.2 mm apart (*i.e.*, the thickness of the simulated adhesive was 0.2 mm) and overlapped by 30 mm. The edges of the overlap were concave semicircular of 0.2 mm diameter and were found to be under tension of varying intensity over their whole periphery.

The maximum tension on this boundary produced the highest shear of the joint in a direction inclined at 45° to the free boundary and the factor of shear stress concentration, or in other words, the ratio of the maximum to the mean shear was calculated from the photoelastic pattern and found equal to 1.81. The factor Δ of this joint can be found equal to 3.75 if $E = 3G$. Thus with the theory of VOLKERSEN the factor of shear stress concentration would be equal to 1.55. The corresponding factor of GOLAND and REISSNER cannot be calculated because the applied tension is not given and the factor k is unknown.

It should be pointed out that a considerable tensile edge stress was present on these specimens: it extended to a depth of about 0.5 mm from the free surface and obviously affected the apparent stress of the free boundary, in particular since this had a radius of curvature of only 0.2 mm and the highest stresses were confined to a depth of the same order of magnitude.

A similar investigation was made by TYLECOTE⁶⁵ on models made of Xylonite 0.12 in. thick in spite of its small stress-optical sensitivity. The members had an overlap of $1\frac{1}{2}$ in. ending in holes of diameter larger than the "gap" between the members, so that all the results are only qualitative in nature. The relative retardations were evaluated from the colours of the isochromatics in white light, recorded on colour film. The colour matching is not a very accurate method, and COKER and FILON working with Xylonite had to use accurate compensation methods or work with "the tint of passage" or sudden change of colour from blue to red at the relative retardation corresponding approximately to the sodium yellow. Furthermore the recording of colours introduces an additional factor of uncertainty. The isoclinics were also recorded photographically, a method not to be advised, as it gives a static picture of these lines, whereas in many cases the isoclinics are faint and unsharp and their exact shape can only be found when they are seen changing position during the simultaneous rotation of polarizer and analyser. The stresses were determined on the circular boundaries as well as in various sections. The highest stress was again found on the boundary which was subjected to a continuous tension, although the isoclinics seem to be accumulating at a small area of this boundary. At such places the isoclinics are most unsharp and if determined by a better method they might well be found to accumulate at a point of the boundary which would be an isotropic point - point of zero difference of principal stresses - and, being on a free boundary where the normal principal stress is necessarily zero, should be a stress-free point. This would be in agreement with the results of the experiments described later.

Experiments of the block-shear test were also carried out on cross-shaped models supported under the horizontal arms and loaded on the vertical bar³⁸. Only shear stresses were considered along the longitudinal sections where the horizontal arms meet the vertical bar: the peak stresses were again found to be at the edges. Photoelastic tests on models similar to plywood test specimens were also made. Fig. 60 shows the high stress concentration arising at the corners of the grooves sawn in the plywood specimens, and show clearly where the failure should start. A critical review of the above tests may be found in references¹⁵ and⁶⁶.



Courtesy of Dr R. V. Baud, Manager, Photoelastic Division, Swiss Federal Institute for the Testing of Materials (EMPA), Zürich.

Fig. 60. Photoelastic patterns of models of standard two-ply (above) and three-ply (below) board test specimens. The crowding of the fringes at the corners indicates the peak stresses developing at these places³⁵.

§ 5. THE ADHESIVE ITSELF AS PHOTOELASTIC MATERIAL

In all the previous experiments the models of the joints consisted of a continuous piece of material machined to the desired shape so that no abrupt change of elastic constants existed at the planes corresponding to the glued faces of the real joints. C. MYLONAS^{15, 66} using the adhesive in a gap joint as photoelastic material, at the suggestion of N. A. DE BRUYNE, was able to achieve a better similarity not only because of the existing difference of elastic constants between adherends and adhesive but also because of the similar behaviour of the model adhesive to the adhesives used in practice. The adhesive used was of the urea-formaldehyde type

known under the trade name of "Aerolite" and was made specially clear and bubble-free as well as extremely slow-setting for these experiments. Wooden gap joints were made as shown in Fig. 61a and slices 2.5 mm thick (Fig. 61b) were cut from them. Of these, some were cut as in Fig. 61c and loaded in shear while one from each joint was used as in Fig. 61d for the determination of the stress-optical coefficient. Unfortunately the setting of the adhesive was irregular faster along the edges and slower in the interior of the joint. As a result the YOUNG's modulus and the stress-optical coefficient were varying throughout and affecting both the stress distribution and its interpretation in terms of isochromatics and therefore these experiments are only qualitative in nature. The adhesive boundary at each end of the overlap had a concave rounded shape due to the contraction of the adhesive during the setting. The variation of the relative retardation in fringes along the boundary of one slice is shown in Fig. 62 at first without any load (setting stresses) and then with a load of 35 lb. applied on the

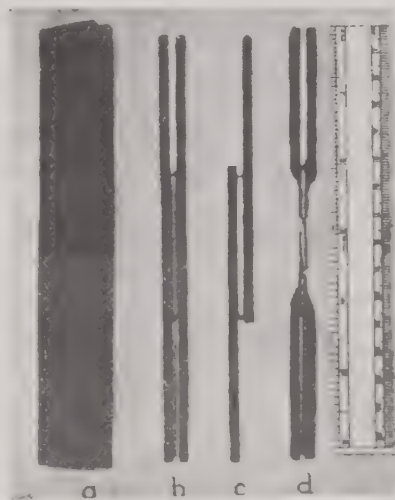
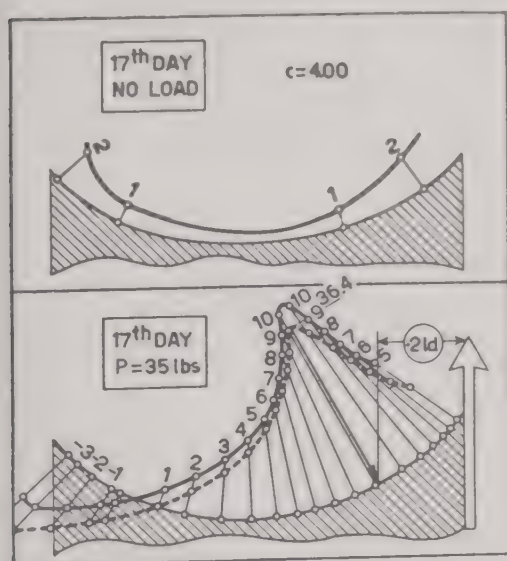


Fig. 61. Wooden gap-joint models made with a urea formaldehyde adhesive which served as photoelastic material: (a) original joint, (b) longitudinal slice 2.5 mm thick, (c) slice as used for shear tests, (d) slice as used for the determination of the stress optical coefficient.



adherend in the direction of the arrow. As both setting and total stresses are necessarily tangential to the free boundary, the former can be subtracted from the latter to give the stresses due to the loading only. The boundary stress has a peak maximum (tension) at about

Fig. 62. The tangential stress distribution along the free boundary of the adhesive at the end of the overlap of the joint of Fig. 61b. (Above) stresses due to setting, (below) stresses due to a load of 35 lb. The peak tension developing at about $\frac{1}{5}$ of the gap from the loaded member is also the highest stress in the whole joint. See also Fig. 63.

1/5th of the gap from the pulled member, then diminishes towards the middle of the adhesive thickness and becomes compressive on the opposite side. The existence of such a peak stress was confirmed by some specimens which started breaking at approximately the same point of the boundary (Fig. 63).

§ 6. MODELS OF JOINTS MADE OF CATALIN 800

In order to avoid the irregularities of stress arising from the setting of the adhesive, C. MYLONAS^{15, 66} made also models of joints of the phenol-formaldehyde plastic Catalin 800. Perfect similarity to metal-to-metal joints would have been achieved if a thin layer of this plastic simulating the adhesive were bonded between two bars of stiffer material. Unfortunately at the time of these experiments no way had been found of achieving this bond without introducing high internal stresses which made the model useless for a photoelastic investigation. Consequently the model



Fig. 63. Confirmation of the photoelastic results by the failure of several specimens which started at the corresponding point.

was machined out of a continuous plate of Catalin, but the difference of rigidity between adhesive and adherends was simulated by the reinforcement of the members (Fig. 64) and by an abrupt change in thickness at the planes corresponding to the glued faces (Fig. 65a). The isoclinics and the stress-trajectories deduced from them are shown in Fig. 65b and 65c while the isochromatics are shown in Fig. 66. Along the boundary of the glue at the end of the overlap the stress is again purely tangential, being tensile on the half towards the pulling member (right) and compressive on the other half, with an intermediate transition point of zero stress. The stress-free condition of this point is indicated by the fact that its retardation is nil; this is confirmed by the isoclinics which converge there, thus showing that it is an *isotropic* point, or in other words a point with equal principal stresses; as the stress normal to the boundary is zero, the tangential must also vanish. The maximum tensile stress (arrow 11) on the boundary is also the highest stress of the whole joint. The

variation of the difference of principal stresses along the line A-A through the point of maximum tension is shown in the curve 1 of Fig. 65d: the variation of the direction of the principal stresses along this line is shown by curve 2. The longitudinal shear along this section is derived from the two previous curves and given by curve 3, and the mean longitudinal shear is given by the dotted line. Thus the factor n of shear stress concentration is:

$$n = 5.4/3.01 = 1.79$$

and the ratio of the maximum tension to the double of the mean shear is:

$$n_s = \frac{11}{2 \cdot 3.01} = 1.83$$

These factors can also be calculated by formulae (3) and (7). As the bolted reinforcing plates shown in Fig. 64 cannot be assumed to adhere rigidly to the members, the values of the factors of stress concentrations were found for the extreme cases of members without any reinforcement as well as for members perfectly bonded to the reinforcement, limits within which the true value must lie. The YOUNG's modulus of Catalin after 10 minutes^{15, 60} of loading has a value intermediate between 100,000 and 200,000 p.s.i. and POISSON's ratio is approximately 0.40 so that the modulus of rigidity G is found as:

$$G = E/2.8$$

Assuming that the "members" have the same width of $\frac{1}{4}$ in. as the "adhesive layer" while their

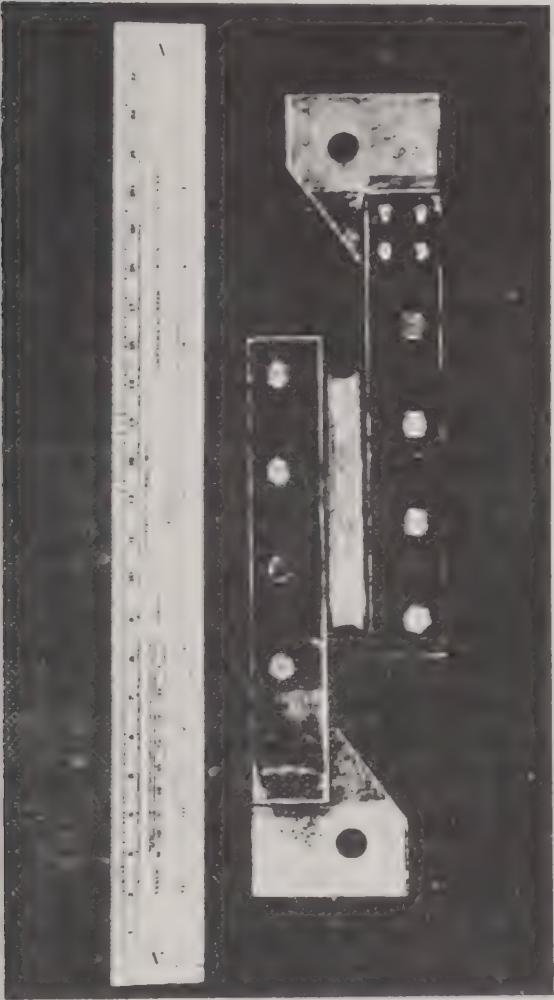


Fig. 64. Model of a gap-joint made of Catalin 800 machined from a solid block. The parts simulating the adherends are reinforced while the "adhesive" is made thinner (see also figur 65a) to correspond to the difference of mechanical properties in real joints.

YOUNG's modulus is correspondingly increased so as to leave their rigidity unaffected, it is possible to calculate the new YOUNG's moduli of the members and the corresponding factors Δ (see formula 2a).

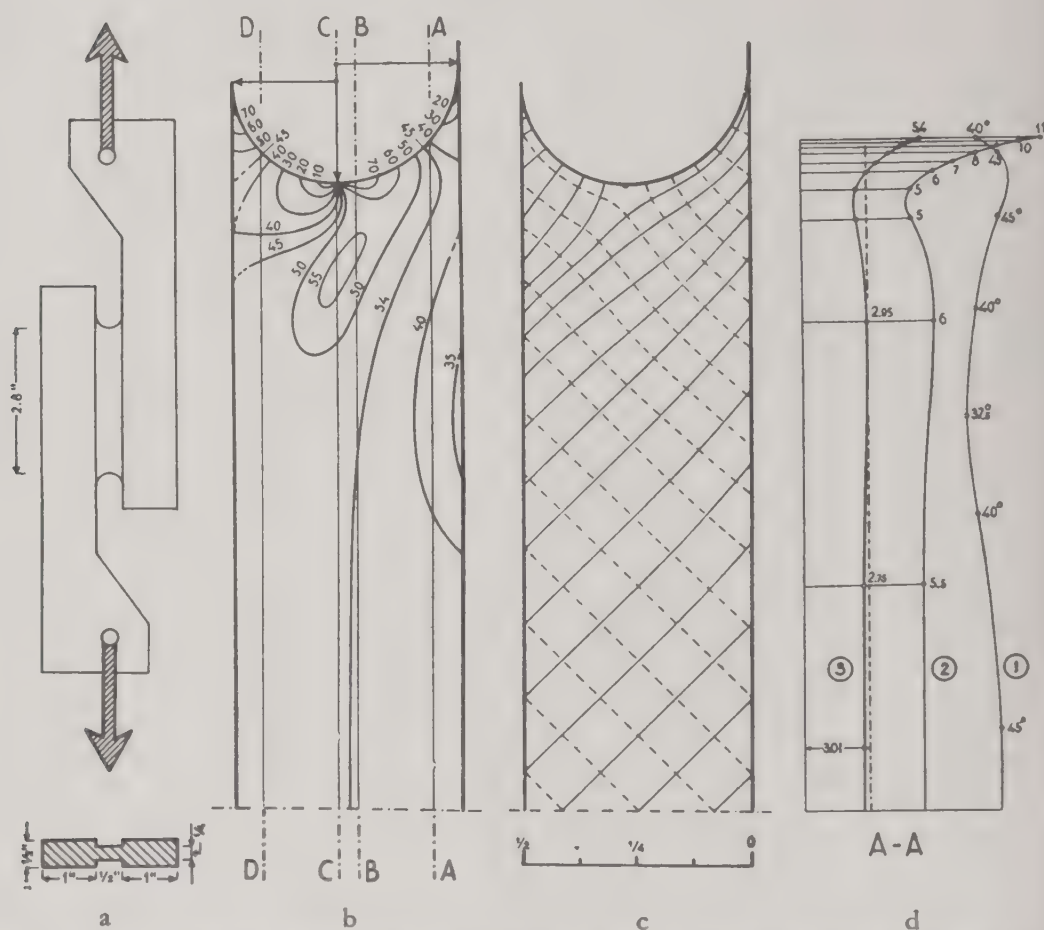


Fig. 65. (a) Shape and dimensions of model of gap-joint made of Catalin 800, (b) isoclinics, (c) stress-trajectories, (d) longitudinal shear distribution.

The theoretical values of the factors of stress-concentration for simple and reinforced members found by formulae (3) and (7) or diagrams 40 and 44 Part I § 6, are compared to the experimental values in Table 12, p. 142. Owing to the great rigidity of the members the factor k (formula 4) is taken as unity.

It should be noted that the theoretical analysis of the joints neglects the thickness of the members in the calculation of the bending moment. This is not permissible with gap joints where this dimension is considerable. A correction can be made by increasing the ben-



Fig. 66. Fringe pattern of Catalin model showing again the development of the highest tension (arrow 11) on the free boundary nearer to the pulling member.

hesive layer is never achieved in practice where the glue is mostly squeezed out of the joint. Nevertheless it is an indication of the inexactitude which may occasionally result from the application of the theoretical formulae.

An extended investigation of the stress distribution in composite joints is now under progress: the joints are made of a layer of a photoelastic plastic simulating the adhesive, bonded between metal adherends, and thus permit a better similarity with actual joints. Tests are also made with joints of large width in which conditions of plain strain are true (see § 2, p. 132). It is hoped that these tests will give a better knowledge of the stresses developing in joints of many types and will lead to methods of reducing them.

ding moment by the ratio $\frac{d+s}{s}$ (Fig. 38, page 97) which is equivalent to taking $k = 1 + d/s$, where d is the thickness of the adhesive and s the thickness of either adherend. In this particular example k will be equal to 1.5: according to formula (7) the factor n of shear stress concentration will remain equal to unity while by formula (10) as well as by the simplified (12) the factor of tearing stress concentration will increase from 0.2 to 0.3.

Thus this experiment shows the existence of a shear stress by some 30% to 80% higher than the highest shear predicted theoretically and, what is more serious, of a tearing stress equal to $2 \cdot 1.83 = 3.65$ times the mean shear whereas theoretically such stress is practically non-existent.

This test is far from conclusive as regards the stresses developing in joints: the model used does not provide exact similarity to real joints and the semicircular boundary of the ad-

TABLE 12

THEORETICAL AND EXPERIMENTAL VALUES OF STRESS-CONCENTRATION FACTORS

	Δ	$n = \tau_{\max}/\tau_{\text{mean}}$			$n_s = \sigma_{\max}/2\tau_{\text{mean}}$	
		VOLKERSEN	GOLAND & REISSNER	Experimental	GOLAND & REISSNER	Experimental
Simple members	2.8	1.40	not valid *	1.79	not valid *	1.83
Reinforced members						
$E_G=10^5$ p.s.i. or $2 \cdot 10^5$ p.s.i.	0.037	1.05	~ 1.00		~ 0.2	
	0.019	1.05				

* Neither of conditions (5) or (6) are fulfilled.

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PART TWO
TECHNOLOGICAL ASPECTS

CHAPTER 5

ORGANIC ADHESIVES

5A. ANIMAL GLUES AND THEIR INDUSTRIAL APPLICATIONS

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§ 1. INHERENT PROPERTIES OF ANIMAL GLUES

The property of animal glue which overshadows that of all other adhesives is its power to change quickly from a fluid state to a firm jelly as a result of a temperature drop of comparatively few degrees. Equally important is its property to reverse this action, due to a temperature rise.

This property of forming a jelly is common to both hide and bone glues, but not to ordinary fish glues. It serves as a basis upon which animal glues are graded or classified. The comparative strength or rigidity of the jelly structure formed from solution at a constant low temperature serves to determine whether a glue is to be classed as high grade or low grade. Viscosities of these same glue solutions are also determined. Glues that have high jelly strengths usually have high viscosities, while those with lower jelly strengths have comparatively lower viscosities. Glues of approximately the same jelly strength usually have about the same viscosity. These two properties, namely jelly and viscosity, serve as the basis for determining the price range of animal glues in the U.S.A.

By virtue of this property of gelation, it is possible for animal glues to effect temporary bonds almost instantaneously. Such bonds soon become permanent. This unique property of animal glues to form temporary bonds so quickly as a result of a temperature drop has placed this adhesive in a class of its own. It has thus made possible the many extremely high speed gluing operations of modern industry, such as the manufacture of paper boxes, assembly of books and magazines, etc., many of which are being produced at rates in excess of one hundred units per minute.

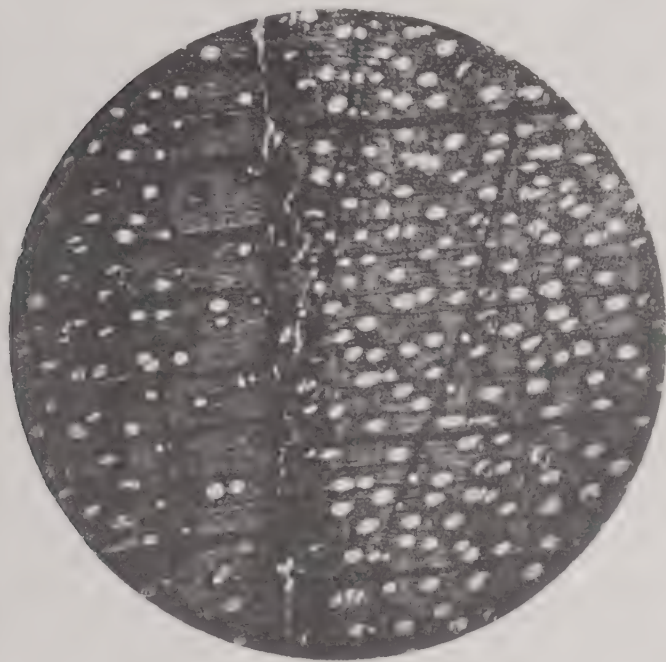
Generally speaking, the basis for adhesion of animal glues can be divided into two classes, namely mechanical and specific. Due to the character of

most surfaces, a certain amount of penetration, on the one hand, is almost inevitable, provided the solution is applied at the normal temperature of 140° F. On the other hand, however, if it was possible to prepare a bond without the attendant penetration, the rupturing force might be surprisingly high. Such a finding would no doubt be contrary to the common conception of the theory of gluing. The average operator in a woodworking plant, for example, holds to the belief that the success of joint making is dependent upon a good glue penetration, both into the exposed pores of the wood and into all other voids produced by machining operations. It is because of this misconception that weak joints often occur in spite of the pains usually taken to control all of the gluing variables.

This mechanical concept of gluing has as its basis a firm anchorage of threads of dry glue extending from one adjoining piece to the other. It is generally conceded that the cohesive strength of a good grade of animal glue is greater than its adhesive strength. As a result, the rupture of the bond of a well glued object would usually not occur within the glue line itself. The adherents of this theory further believe that if the glue is properly anchored in the small cavities of adjacent pieces to be joined, the shrinkage of the glue upon drying will draw the pieces together so firmly that any imperfection in machining the surfaces, any tendency toward change in physical dimensions brought on by improper moisture contents of the pieces and any smaller defects may be of little consequence. In his great zeal to bring about undisputable anchorage through penetration, the operator too often destroys the connecting link, the glue layer, between the two pieces. The use of excessive pressure, too thin a glue solution, too high a temperature of solution, and objects to be glued that are too warm, all of these factors, alone or combined, will assure glue penetration, but at the same time will produce a discontinuous glue film which always results in a weakened bond.

From the foregoing, it is quite evident that a glue operator must be cognizant of factors other than those of mechanical adhesion in order to be able to use animal glue to best advantage. The principal additional factor is commonly referred to as specific adhesion or sometimes molecular adhesion. It pertains chiefly to the ability of a glue to attach itself firmly to smooth, hard surfaces unlike the porous type just discussed. That animal glue will stick to surfaces which it cannot penetrate is demonstrated by the drying of a glue solution on a clean glass surface. It will usually be found that sufficient force is exerted by the drying and contracting of the animal glue to pull away portions of the glass surface, thereby producing a frosted or chipped effect.

TRUAX¹ proved by means of photomicrographs that while glue may be made to anchor into wood by filling the cell cavities and finally drying, there is no penetration beyond this point. The solution does not pass through the cell walls, yet the glue clings to the cell walls (see Fig. 67 and 68) forming a coating of dried glue inside each of the pores



*Courtesy of Forest Products Laboratory,
Madison, Wis., U.S.A.*

Fig. 67. Photomicrograph of cross section through two pieces of maple showing the dried glue clinging to the cell walls.

rather than a shriveled thread as one might suspect if the adhesion were solely mechanical. This bond formed between the glue film and the cell wall is strong enough to tear or break the latter whenever an attempt is made to separate them.

It would seem, therefore, that equally as important as mechanical adhesion or bonding is this specific affinity of animal glue for many other surfaces, including wood, glass, etc. An interesting electronic, positive and negative charge, theory has also been advanced to ac-

count for this adhesiveness of animal glue to such impervious materials as glass whose surfaces exhibit an alkaline reaction. Briefly, the thought is that the negative charges of the molecules of the alkaline surfaces attract the positive charges of the amino groups of the animal glue molecules. GERNGROSS and GOEBEL² in supporting this specific adhesion theory, suggest the possibility of the chemical protein groups exhibiting molecular attraction during the pressing of the glue, while mobile. They point out that when the free amino groups are fixed or set in the protein by formaldehyde after application of the hot animal glue solution to the surfaces to be bonded, no weakness is apparent. (See Composition Cork, p. 155, for application). These authors also point out that all of the commercial adhesives possess high molecular weights and that some, animal glue for example, embody

extended chain molecules bound crosswise by partial valences. These chains are capable of arranging themselves in such a manner that their axis of length is parallel to the pull of the rupturing stress. The purer forms of animal glues, the least hydrolyzed, are best examples of the phenomenon. Studies of Röntgen diagrams of animal glue films under stress show that



*Courtesy of Forest Products Laboratory,
Madison, Wis., U.S.A.*

Fig. 68. Photomicrograph of longitudinal section through two pieces of maple showing the dried glue clinging to the cell walls.

these chains referred to above arrange themselves perpendicular to the glued surfaces in order that the strains in the bond occur in the direction of the chief valence bonds rather than in the direction of the weaker secondary valence bonds.

In addition to glass, as an example of the quality of specific adhesion of animal glue, there is an equally good example of the same property exhibited in the use of this adhesive to bond abrasive particles in the manufacture of coated abrasives and

“set-up” wheels which will be discussed later. (See p. 163).

The gluing of impervious surfaces, however, represents the minority group of the various types that are bonded. Most gluing jobs in fact, involve the use of materials of a more or less fibrous nature. In most of these cases the glue solution penetrates into the surface in varying degrees but sufficient in each case to produce a sound bond. In case of surfaces that are exceptionally porous, a presizing with glue is necessary before efficient bonding can be satisfactorily effected. Photomicrographs of paper bonds, common to the paper box industry, have shown that the glue had enveloped all of the surface fibers. In case of labels on which hot glue has been spread, prior to application to another surface, the penetration was appreciable. A study of paper joints in general has forcibly brought out the necessity of completing the assembly before the freshly spread hot animal glue solution

jellies or otherwise loses its tack, thus preventing good contact. Blistering of labels is a good example of this fault as it is invariably due to the glue's setting while in poor contact with the base material, or where it did not make contact at all. Examinations of all sections where good contact was effected before congealing of the glue film occurred revealed bonds that were in all cases stronger than the paper itself, even though the glue was in contact with only the surface fibers of the paper. The necessity of bringing pressure to bear between surfaces to be bonded with a hot animal glue solution before the latter has had a chance to pass into the jelly stage applies generally to all industrial applications of this adhesive.

§ 2. PREPARATION AND HANDLING OF GLUE SOLUTIONS

Before discussing the many applications of animal glues in industry it would be advisable to consider some of the recommended procedures for

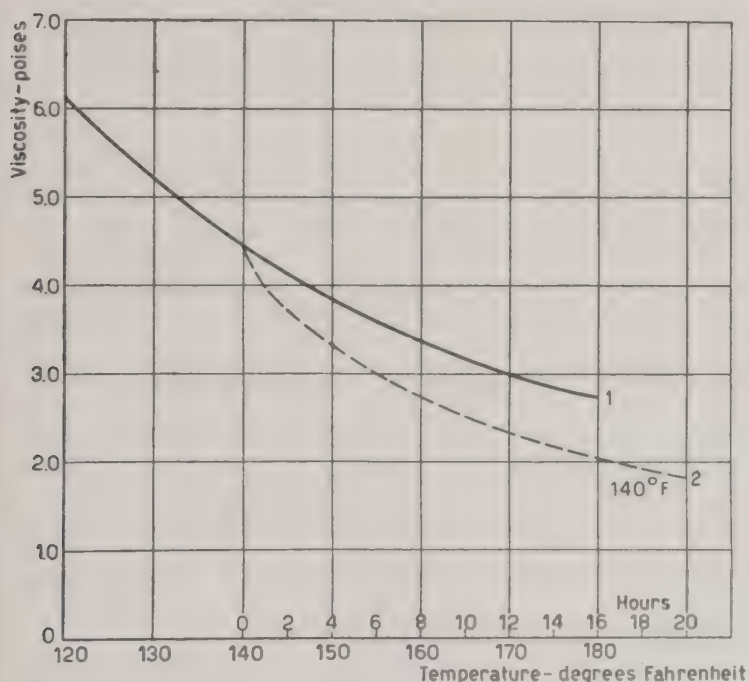


Fig. 69. Curve 1: Effects of temperatures on viscosity of a $2\frac{1}{4} : 1$ (30.8 %) solution of a 104 millipoise hide glue.
Curve 2: Effects of holding time on viscosity of same glue at 140°F .

the preparation and handling of this adhesive. These suggestions will apply in general to the preparation of animal glue solutions for use in all industries, with few exceptions.

At least two or three generally accepted procedures for putting dry animal glue into solution should be considered. These methods will differ according to the physical form and grade of the glue, concentration to be

prepared, and type of mixing equipment available.

A generally accepted method is that of mixing ground glue, usually ground flake, into cold water, always using a definite weight of each. The

mixture is agitated until all glue particles have become wet, after which the mix is allowed to stand for one to two hours, depending upon the particle size of the glue, the grade of the glue and the concentration being prepared. After the soaking period, the glue is melted down by the application of heat in a jacketed container. This method has its disadvantages, however, especially when mixed in large batches in a container fitted with a mechanical

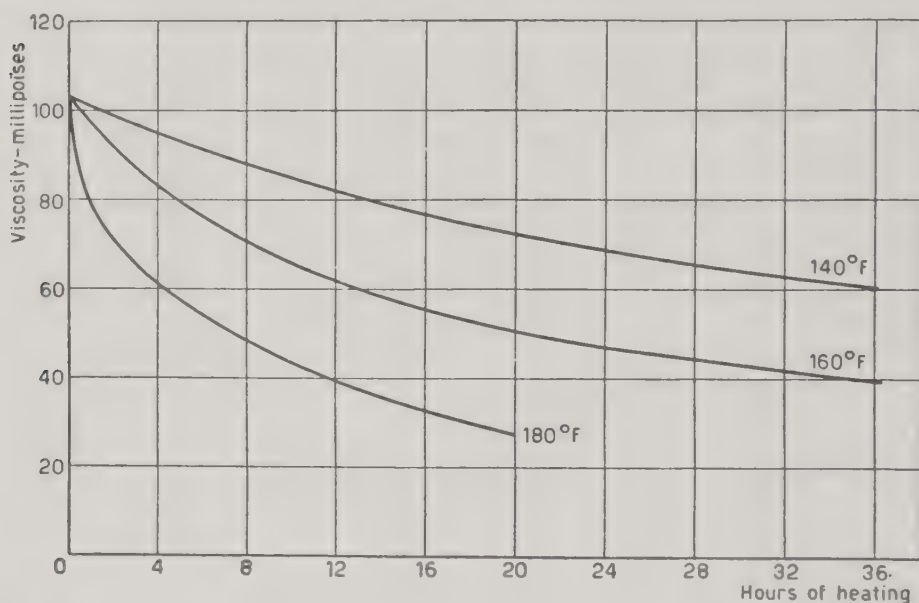


Fig. 70. Effect of holding temperatures on the viscosity of a 102 millipoise hide glue solution of a 12½% concentration.

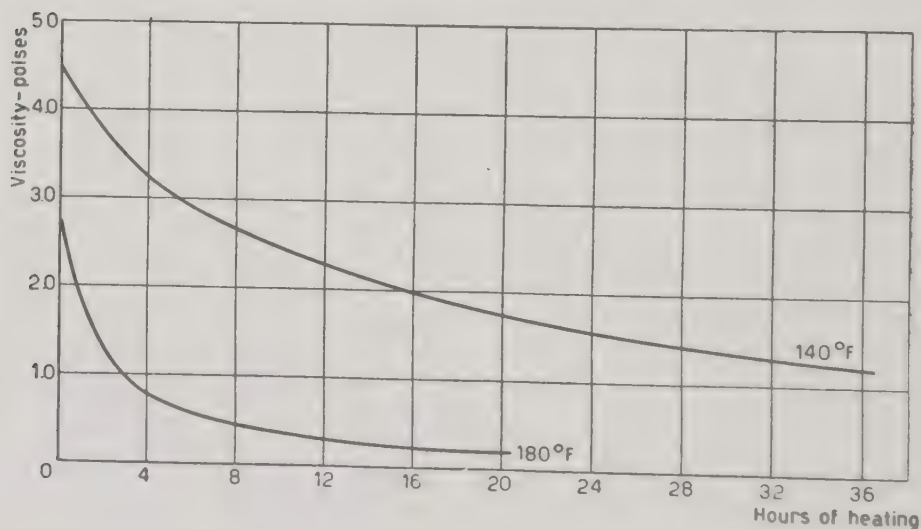


Fig. 71. Effect of time and temperature on viscosities of a 2¼ : 1 (30.8%) solution of a 104 millipoise hide glue.

agitator. At high concentrations the swollen mass may form such a firm jelly that the agitator cannot be run.

A more practical method and one very generally used with mechanical mixers is as follows: Place the proper weight of cold water in the mixer, start the mixer going and slowly add the correct, weighed amount of dry glue. As soon as all of the glue has been added, gradually turn on the heat

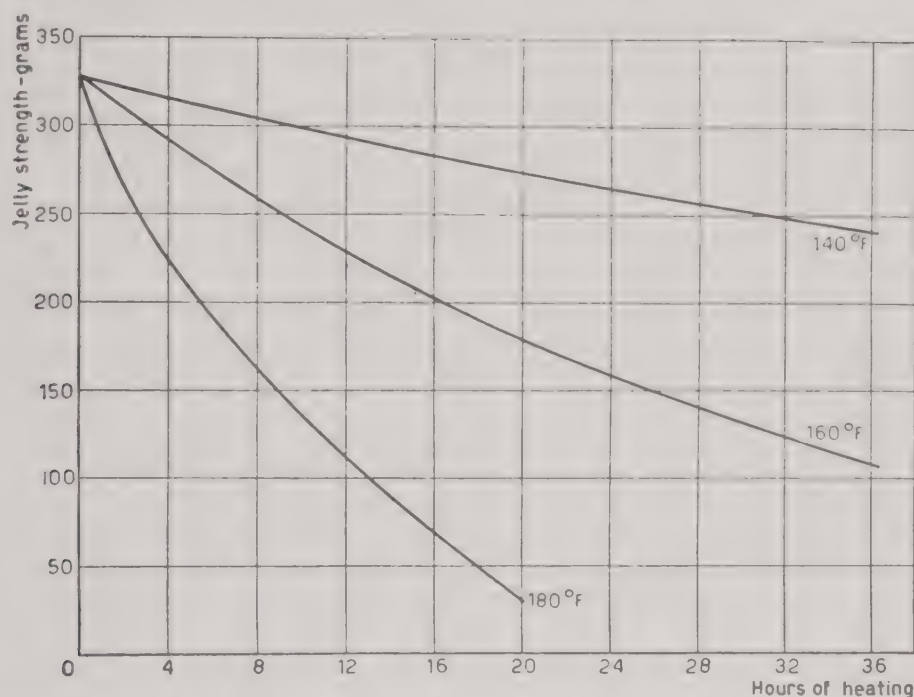


Fig. 72. Effects of time temperature on jelly strength of a $12\frac{1}{2}\%$ solution of a 324 gram hide glue.

and allow the mix to warm up as it goes into solution under constant agitation. Make sure that the glue solution being prepared is not heated above 140°F .

When it is desired to prepare very heavy solutions of high testing hide glues or to prepare the hot solution for use as soon as possible, this can be accomplished by a slight alteration in the above procedure. Fill the converter with the required weight of hot water, 180 to 185°F . so that the temperature after crutching in the required weight of dry glue will be approximately 140°F . but no higher. Continue the agitation at this temperature until complete solution has been effected. When prepared in the same container, the hot-water method will permit a glue solution to be prepared in about one-half the time required when starting with cold water. Constant agitation is absolutely necessary when preparing a glue solution in accordance with

this last procedure. A double acting agitator is preferred, that is one composed of two separate sets of blades, one turning clockwise and the other counter clockwise. One of the sets of blades should sweep and practically touch both the sides and the bottom of the container. The most efficient type of heat to use in the jacket is steam under partial vacuum. Efficient converters, however, are made with electrically heated jackets. In all cases the heat should be thermostatically controlled and the holding temperature should not exceed 140° F.

Maintaining the prepared glue solution at a maximum temperature of 140° F. cannot be too strongly emphasized. The detrimental effects resulting from overheating glues should, therefore, be strongly impressed upon the operator. Such temperatures, in excess of 140° F, cause rapid hydrolysis or breakdown of the glue molecules and result in a rapid drop in the viscosity of the solution as shown in Fig. 69, 70, 71 and 72.

With all animal glue solutions the rate of hydrolysis increases with an increase in temperature, varies inversely as to the concentration, and proceeds more rapidly with high grade glue than with low, that is, the higher the grade of glue the more rapid will be the rate of hydrolysis.

Hydrolytic decomposition reduces both the jelly strength and the viscosity of a glue solution. Usually the viscosity drops faster than does the jelly. A decrease in the jelly strength of a glue is evidenced by a progressively slower setting time after spreading. The effect is further shown by a lowering of the tensile strength and finally by a decrease in the pliability of the dried film.

The foregoing points have been enumerated to show why glue solutions should not be mistreated by overheating, provided one wishes to obtain maximum strength and the original toughness of the adhesive.

A last warning should be made regarding the recommended minimum holding temperature for animal glue solutions. This figure is set at 125–130° F. since glue solutions held for any appreciable length of time at temperatures below this value may readily be attacked by bacteria. This is particularly true of the more dilute solutions. A suitable preservative such as the chlorinated phenols or cresols should be added; about 0.1% basis the weight of a dilute solution (below 25%). This amount may be altered somewhat, however, according to such variations as holding time and temperature.

It is hoped that suggestions presented in the foregoing will help the users of animal glue to be able to use it to better advantage and thereby obtain more efficient results.

The jelly and viscosity tests of animal glue as referred to herein were all

Composition and Colloidal

PRINTERS ROLLERS	CORK — GASKETS CLOSURE CAPS SHEETS INSULATION	MATCHES — BASE TIP STRIKING ABRASIVE
WOOD COMPOSITION — HEELS SMOKING PIPES TOYS	RUBBER — TIRES FOOTWEAR SYNTHETIC MECHANICAL	DUPLICATING COMPOUNDS — HECTOGRAPH
ELECTROLYTIC METAL REFINING	DOLLS — DISPLAY FORMS	PLASTERCAST MOULDS
CERAMICS	PROTECTIVE COLLOID IN WATERPROOFING EMULSIONS	DYEING BLEACHING AND CLEANING COMPOUNDS
PICTURE FRAME AND DECORATIVE MOULDING	MOULAGE	ASBESTOS PIPE
ARTIFICIAL LIMBS	EMULSIFYING AGENT	FIREWORKS
CLARIFICATION — WATER CHEMICALS	LEATHER DRESSING AND POLISH	EMULSION STABILIZER
ARTIFICIAL FLOWERS	GRAINING ROLLERS	SANDBLASTING PROTECTIVE COATING

Adhesive

WOOD — FURNITURE DISKS TABLES CHAIRS CASKETS CABINETS MILLWORK PENCILS BOARDS PATTERN MAKING TOYS FISHING RODS	GUMMED PAPER AND CLOTH — STAY PAPER SEALING AND VENNER TAPS LABELS — ENVELOPES — MULTIPLE BAGS
MUSICAL INSTRUMENTS — PIANOS ORGANS WOODWIND STRING ACCORDIONS	BOOK AND MAGAZINE BINDING — BACKING CASEMAKING PADDING LOOSE LEAF BINDERS
ADVERTISING DISPLAYS	AMMUNITION CONTAINERS
PARATROOPER KITS	LEATHER BELTING
LUGGAGE — LEATHER CANVAS RAWHIDE	ICEPROOF LABELING

Sizing and Coating

RAYON — VISCOS ACETATE CUPRA SPUN — SLASHING AND FINISHING	PAPER — WRITING BOND CURRENCY MAP — BLUEPRINT ONIONSKIN COATED PLAYING CARD WALLPAPER CREPE TWINE	GASKETS — FIBRE ASBESTOS PAPER
SILK FINISHING	HATS — STRAW AND CLOTH	CALCIMINES — HOT AND COLD WATER PAINTS
COTTON FINISHING	WOODEN ALCOHOL BARRELS	WALL SIZES
WOOL SIZING	PRINTED ADVERTISING TAPE	GREASE AND OIL CONTAINERS
CAMOUFLAGE CLOTH AND NET	LACQUER UNDERCOAT	GLASS CHIPPING
WINDOW SHADES — CLOTH AND PAPER	REED FURNITURE	DECALCOMANIA
RUG & CARPET SIZING		TURPENTINE BARRELS
		PAINT CONTAINERS

Chart of the uses of animal glue.

determined according to the *Standard Methods for Determining Viscosity and Jelly Strength of Glue*, as published in the United States by the National Association of Glue Manufacturers, Inc. For those who care to look into the detailed procedures for making these tests, references ^{3, 4} are given.

§ 3. USES AND GENERAL DISTRIBUTION OF HIDE AND BONE GLUES

The accompanying Chart (p. 155) was prepared and furnished by the National Association of Glue Manufacturers, U.S.A.

Table 13 shows the percentage of the total weight of hide or bone glue used by each class of industry in the U.S. during the year 1943 while Table 14 shows the percent of the combined totals of hide and bone glues used by each group during this same period.

TABLE 13

SALES DISTRIBUTION OF HIDE AND BONE GLUE

According to the amounts reported used by various industries during the year 1943

Hide glue		Bone glue	
Industry	% of Total Used	Industry	% of Total Used
Abrasives	17.1	Gummed Paper & Cloth	49.8
Wholesale Jobbers	11.0	Wholesale Jobbers	11.3
Adhesives	9.8	Adhesives	6.3
Textiles	7.1	Chemicals	5.5
Paper Manufacturers	6.8	Paper Manufacturers	3.5
Wood Working	6.6	Miscellaneous	3.5
Furniture	6.5	Paper Products	3.4
Matches	6.1	Paper Boxes	3.2
Cork Gaskets	4.7	Calcimine	1.7
Gummed Paper & Cloth	4.5	Textiles	1.6
Polishing Wheels	3.3	Woodworking	1.6
Miscellaneous	3.1	Export	1.6
Paper Products	2.5	Rubber	1.3
Printed Rollers	1.9	Bookbinding	1.1
Paper Boxes	1.8	Cork Gasket	1.1
Book Binding	1.7	Luggage	0.9
Chemicals	1.2	Ammunition Shell Containers	0.6
Wall Paper	0.9	Abrasives	0.5
Ammunition Shell Containers	0.8	Boxes, Wood-Fiber	0.4
Calcimine	0.8	Wall Paper	0.3
Boxes Wood-Fiber	0.7	Polishing Wheels	0.3
Export	0.4	Furniture	0.3
Luggage	0.3	Barrel Sizing	0.2
Barrel Sizing	0.2		
Rubber	0.2		
Total	100.0%	Total	100.0%

TABLE 14
SHOWING WEIGHTED COMPILATION OF THE HIDE AND BONE GLUE
COLUMNS IN TABLE 13

Industry	% of Hide and Bone Glue Used in 1943
Abrasive	9.0
Adhesives (Compounded)	8.1
Ammunition-Shell Containers	0.7
Barrel Sizing	0.2
Book Binding	1.4
Boxes, wood-fiber	0.6
Calcimine	1.2
Chemicals	3.3
Cork Gaskets	2.9
Exports	1.0
Furniture	3.4
Gummed Paper and Cloth	26.9
Luggage	0.6
Matches	3.1
Miscellaneous	3.3
Paper Boxes	2.5
Paper Manufacturers	5.2
Paper Products	2.9
Polishing Wheels	1.8
Printers' Rollers	1.0
Rubber	0.7
Textiles	4.4
Wallpaper	0.6
Wholesale Jobbers	11.1
Woodworking	4.1
Total	100.0%

§ 4. INDUSTRIAL APPLICATIONS OF ANIMAL GLUE

In view of the many industries and uses listed in the Chart (p. 155) and Tables 13 and 14, it is quite evident that it would be impossible to describe each individual application in any detail within the scope of one chapter. Instead, the discussion will necessarily be limited to a few of the representative industrial operations that consume the major portion of the animal glue production.

Many industries prefer to use animal glue in its natural state, that is, without the use of additives. High tensile strength, toughness and rigidity are uppermost in the requirements of an adhesive for this class of industry of which the abrasive and woodworking fields are representative. These qualities are not suitable, however, for many industries. By the addition of plasticizers, tackifiers, liquefiers, defoamers, tanning agents, etc. the scope of usefulness of animal glue has been greatly extended.

Additions of glycerin and glycols, for example, lend permanent flexibility to the glue film, necessary in bookbinding 'printers' rolls, rayon sizing, etc.

Additions of sugar products and dextrans do not impart flexibility but do prevent animal glue films from warping on drying. These glues find use in paper box plants, for example, where flexibility is not required but a non-warping glue film is necessary.

Additions of chemicals that have a liquefying effect upon animal glues prolong the tackiness of their films. Glues of this nature are required by the luggage trade, for example, where the assembly period may require as long as thirty minutes.

Foaming is a natural quality of animal glues and is used to advantage in the manufacture of matches, preparation of emulsions, etc. Industries using high speed mixing and spreading equipment, however, require foamless glues. It is necessary to add defoamer to glues in order to meet this latter requirement.

Many industries require an adhesive possessing the general working characteristics of animal glue, but one which will become highly water-insoluble after bonding. This can be accomplished by the addition of tanning agents such as ammonium bichromate, alum or formaldehyde. Such additions make animal glue suitable for use in the lithographic industry and for composition cork.

Where jellying is a disadvantage, sufficient liquefiers can be added to produce a glue that can be used at room temperature. For this purpose one may add urea, thiourea, ammonium nitrate or other liquefying agents.

(a) *Gummed Paper and Cloth*

It may be noted in Table 14, p. 157, that more animal glue is consumed in the manufacture of this particular commodity than for any other single class of products. Of all the glue produced in 1943, 26.9% was used in the manufacture of gummed paper and cloth. By far the majority of the glue consumed by this industry was bone. The reason is quite evident when one considers that only the low testing (low jelly strength) glues are cold water soluble. A glue must have this characteristic in order to produce a good gummed paper. One of the important requirements of a good gummed paper is the immediate development of tack or grab after being remoistened. Bone glue imparts these necessary qualities to gummed paper. For this reason, it is practically the universal adhesive used in the manufacture of this product.

In order to acquire this rapid remoistening and setting qualities in a

gummed product the manufacturer may find it necessary at times to add certain ingredients to his heavy glue solution before coating the paper, in order that the finished product will meet specifications. Materials commonly added for this purpose are: fish glue, liquefied animal glue, and possibly glycerin.

It must be considered that all animal glues are somewhat hygroscopic; that is, they exhibit a moderate affinity for water or moisture from the air, especially under conditions of high humidity. This, however, is one of the qualities of animal glue that helps to make it the preferred adhesive for all remoistening gummed products. If the humidity becomes too high where the tape is stored or if an excess of ingredients have been added for the purpose of improving the wetting properties of the product, making it more hygroscopic, then the glue film is more likely to absorb sufficient water to impart tackiness to the adhesive layer. Adhesion to adjacent layers occurs and upon drying out a permanent bond is formed. The tape is then said to be "blocked" and is of little or no value. It is only through experience that one can judge the proper amounts of such additives to use in order to improve the adhesive qualities of the product without causing it to become too hygroscopic.

After the glue solution of about 50% concentration has been prepared so that the finished product will meet requirements, it is added to the coating machine. Here it is applied to a continuous sheet of paper that ultimately becomes a gummed product.

The sheet of paper to be gummed may vary in width from about 27 to 72 inches and travels through the coating rolls at a rate of 200 to 400 feet per minute. A perfectly even coating of the correct amount of glue on the paper web is necessary before it is subjected to the drying operations. The amount of glue applied will generally average from 20 to 25% of the weight of the finished product.

The gummed sheet must then be dried. This is a very important operation and improper handling will produce an unsalable product. It may be badly warped or it may block after being rolled up, due to insufficient drying even though the gumming composition was properly prepared. A few suggestions that may help to prevent some of these undesirable qualities are:

- (1) The warm glue film should not be hit with a hot blast of air immediately after being spread. This will usually cause case-hardening or a glazing over the glue film and thus hinder subsequent drying.
- (2) During the drying operation the gummed sheets should be kept taut or tensely stretched at all times to preclude the glue from warping the sheet as it dries since glue contracts appreciably upon the loss of water.

(3) Suggestions have been made by some operators that it improves the drying rates of glue films to first jell them, thus forming a micellar or net work structure which then serves as a means to keep the film more or less open during the subsequent drying period. This, however, is not standard practice, no doubt due to the mechanical difficulties that would be encountered in first chilling the film, then preheating it before entering the drier. A glue film which has been dried from a jelly may not make as good a gummed product as would one that has been dried without going through a jelly stage. This thought is based upon the fact that when a glue, dried from a jelly, is immersed in water it will absorb an amount of water in proportion to the water content of the jelly from which it was dried. In other words, a glue dried from a jelly containing 10% glue will, when immersed in water, absorb more water than will the same glue which has been dried from a jelly containing 50% glue. Likewise, a glue dried from a 50% jelly will absorb more water than will the same glue which had been dried without going through the jellied stage. The latter condition approximates that of gummed tape. Such a glue, dried without going through a jellied stage, will not absorb water as will glue which has been dried in the conventional manner, but instead will dissolve slowly from the surface only. This is looked upon as an advantage for gummed papers.

The adhesive layer of a gummed product should not be penetrated all the way through by the remoistening liquid. When this occurs it usually results in the adhesive layer being mostly removed. This action would probably occur much more often with a glue film that would readily absorb water as compared to one that would not absorb water so readily. If, however, the adhesive film of a normally dried product is consistently removed by the remoistening operation, it usually indicates that the layer of dried glue on the tape is too thin.

Most commercial gummed paper is dried by first passing the sheet over steam heated rotating drums in order to preheat the glue layer before it enters the glue drier where it usually passes through consecutive, increasing stages of heat with air at comparatively high velocities. It emerges at a fairly high temperature in a perfectly dried condition. This whole drying operation is of comparatively short duration, consuming not more than one minute.

Leaving the drier, the gummed sheet is passed at a rather sharp angle over three bars respectively. One is located at right angles to the direction of the paper, one is 45° to the right of the paper direction and the third is 45° to the left. Passing over these various angles puts millions of tiny cracks in the glue film on the surface of the coated sheet. Such a condition

serves at least a two-fold purpose. First, the sheet is made quite flexible and as a result greatly facilitates subsequent handling operations by reducing the tendency to curl. Second, water will penetrate or dissolve the film faster through the broken surfaces of these fractures than through the originally dried surface, due to more or less case-hardening of the latter. This second reaction results in a more rapid wetting of the film and ultimately a quicker development of tack, a very important quality of a good tape.

As previously mentioned, the bulk of gummed tape is made with a low testing bone glue, since its rate of developing tack with cold water is of greater importance than its ultimate tensile strength. There are, however, certain operations where strength of bond is an important requirement. An example of this is the gummed cloth (sisal) which is used on the corner construction of fiber boxes. This tape must withstand unusual strains. A similar type, prepared from a heavy kraft paper, is used in binding the corners of smaller boxes. Such tapes are coated with a blend of medium testing hide and bone glues, the grades depending upon the requirements of the end use.

Whenever the test of the glue appreciably exceeds that used on ordinary sealing tape it is usually necessary to use warm water as the remoistening agent in order to produce the proper tack as such glues are usually not soluble in cold water. It has been found that in many cases the addition of a product such as dextrine to remoistening solution improves its wettability and thus improves the bonding qualities of the tape.

(b) *Surface-Coated Abrasives*

Surface-coated abrasive products in which animal glue is used as a binder comprise some 400 different items. These include specific types and weights of backing, specific types of abrasive, and abrasives of different particle size classification.

Fabrication of coated abrasives depends upon the use of a satisfactory adhesive. Animal glue proved itself long ago to be the most efficient adhesive for this particular industry. Some of the principal reasons for its selection are: (1) rapid set due to its jellying property, (2) specific adhesion to the surfaces of the abrasive particles, (3) toughness of film, (4) resistant of the dried film to shock, (5) durability of the bond when stored under favorable conditions, (6) economy of use, and (7) ready availability.

In the manufacture of surface-coated abrasives animal glue is applied in two separate coatings. The first coating, called the "maker-coat", is applied

to the desired backing as a heavy solution of a high testing, high tensile strength hide glue. The solution may be as heavy as 50% concentration, depending largely upon the particle size being coated. The purpose of this first coating is to anchor the abrasive particles to the backing. The glue as applied must be as free from foam as possible. The application of glue to the backing is similar to that of gummed paper and cloth.

Immediately after an even coating of the hot glue has been applied to the backing the proper amount of the desired abrasive is applied. At this point the adhesive must exhibit the following characteristics: It must first be sufficiently fluid to permit the abrasive particles to imbed themselves. It must "wet" the surfaces of the abrasive particles as well as the backing, thus insuring good bonding qualities. Very shortly after the abrasive becomes imbedded in the adhesive layer, the latter must set or become firm in order that the coated sheet can be handled without fear of disturbing the orientation of the abrasive particles. Animal glues have these qualities.

After the glue has set sufficiently to permit handling, the coated sheet is sent through a preliminary drying zone. This operation further sets up or strengthens the glue-abrasive-backing combination. It is then ready to be sent through a second glue-coating machine called the "top-sizer". A much lighter glue solution is applied at this time although the same grade of glue as used for the "maker-coat" is generally used. This coating is applied to the surface of the abrasive for the purpose of binding more firmly the loosely held surface grit which is not securely held by the "maker-coat."

Leaving the "top-sizer", the coated sheet is passed into a second drying compartment where it is completely dried. The proper removal of moisture from this finished sheet is an important operation. Quite in contrast to the method previously described for removing moisture from a sheet of gummed paper (see p. 159), this operation is necessarily a much slower one. The principal reason for this difference is the much heavier coating of glue to be dried; also the fact that this glue layer is being dried from a jelly. As the coating is much heavier, it means that greater difficulties will be encountered with warping if the sheet is dried too rapidly.

Since the glue on coated abrasives has been set by the congealing of the glue, too much heat in the drying operation would cause the adhesive to soften sufficiently to disturb the orientation of the abrasive particles and thus damage the quality of the finished product. As a result, the two most important conditions that must be kept under control during the drying operation are temperature and humidity. The drying temperature must be kept sufficiently low so as not to soften the adhesive layer. As the drying

progresses, however, the softening point of the adhesive correspondingly increases, thereby permitting the temperature to be increased.

During the drying operation the humidity of the air should be controlled to permit economical drying and at the same time prevent casehardening of the adhesive layer. A controlled drying rate avoids formation of strains within the glue film and between the glue-abrasive interface. Casehardening occurs when drying is too rapid or the relative humidity is too low. As a result, the pores of the surface of the adhesive become sealed and thus measurably decrease the drying rate. When the humidity is too high, on the other hand, the rate of drying is decreased. The optimum conditions for any one particular plant would, therefore, have to be determined, as it would depend upon available equipment and methods of operation.

Although by far the bulk of coated abrasives are still made with animal glue as a binder, there has been a trend in recent years toward the use of synthetic resins. Today, one of the general uses of such resins is as a "top-size" over an animal glue base coat. However, when highly water resistant coated abrasives are required, they are usually bonded with straight resin. The resin used is always of a thermosetting nature and usually of a phenolic type.

Another departure from the use of straight animal glue is the use of a mixture of the latter with an inorganic filler such as marble dust. This combination is described in U.S. Patent 2,322,156. Such coated abrasives find use in the preparation of sanding discs where high temperatures are encountered while in use.

(c) Polishing Wheels

Although resins are used almost exclusively as a binder in grinding wheels, animal glue is still the preferred adhesive for making polishing or "set-up" wheels. Accurate control of temperature and humidity is just as important in this operation as in the fabrication of surface-coated abrasives. Considerable progress has been made toward the control of atmospheric conditions in the wheel "set-up" room. Polishing room men are quite climate conscious. Thermometers and hygrometers to measure the temperatures and the amount of moisture in the air respectively have become standard equipment. Air conditioning and dehumidifying units have done much to eliminate difficulties formerly caused by excessive humidity.

Glue is equally sensitive to cold and heat and as a result, uniform temperature must be maintained in order to have polishing wheels set properly. Experience has shown that a temperature of 80° F and a relative

humidity of 45 to 55% provides ideal "set-up" conditions. In addition to constant temperature and humidity, the polishing room must be free of drafts and so arranged that glue can be applied to the wheel and the entire set-up operation carried out as quickly as possible to prevent the glue from congealing during this operation. A glue that is permitted to jelly during the assembly operation results in a poor adhesive since the grain will not adhere to a jellied glue layer.

Draft may cause the glue liquor to congeal even in the short interval between the time the glue is removed from the pot by a brush and applied to the face of the wheel. Accordingly, the layout of the polishing room will require that windows and doors be "draft-proofed," and that the polishing wheel be placed as closely to the glue pot as possible. The hot glue solution is applied to the face of the wheel, usually with a brush, and the wheel immediately rolled in a trough of abrasive grain until it has picked up all the grain that it will hold. The glue coating will pick up grain in proportion to the amount of pressure that is applied in rolling the wheel through the trough. It is necessary, therefore, to maintain uniform pressure in order to achieve uniform polishing results.

Temperature is still a controlling factor when glue is again applied to the face of the wheel now covered with abrasive grain. A cold surface, for example, coming in contact with a hot glue film will cause immediate gelation and thus markedly reduce the ultimate bonding power of the glue. Actually, the action is similar to that of a cold draft striking the glue and the ultimate results are the same, that is, the glue loses much of its bonding power and shrinkage-cracks may develop across the face of the wheel head.

In order to eliminate this danger, provisions should be made in the polishing room to warm both wheels and abrasive grain to temperatures of 100 to 120° F. When the wheel head components are thus heated, glue can be safely applied at its normal holding temperature of 140° F.

One may question further the reasons for heating or warming the wheel and abrasives. First, it allows the glue to set slowly and naturally instead of causing it to congeal quickly. Slow setting allows glues to attain maximum strength under normal conditions. Too rapid chilling or congealing of the glue does not allow for proper penetration, causing weakness of bond which may result from lack of contact, or poor contact; from poor adhesion due to the inability of the chilled glue to "wet" or bond to wheel or grain; from internal stresses set up when drying an excessively thick layer of glue.

After the completely fabricated set-up wheel is transferred to the drying room, atmospheric conditions are still subject to control to insure that the

dried wheel will be free from defects that will otherwise result in short life or sub-standard quality.

Animal glue is a reversible colloid; that is, it is capable of alternately jellying and melting. It also has the ability to absorb or release moisture. In cold water while soaking, for example, it may absorb as much as ten times its weight of water. Glue, however, attains its maximum tensile strength when its moisture content is in the range of 10 to 14%. Thus both temperature and humidity of the drying room are so adjusted as to allow the set-up wheel to reach this level of maximum strength. Such conditions for ideal drying have been found to be about 85° F and 50% relative humidity, although satisfactory results have been obtained from wheel drying rooms held at 75° F and 45% relative humidity as well as 90° F and 55% relative humidity.

When proper drying conditions are maintained, most single coated polishing wheels can be satisfactorily dried within 24 hours and double-coated wheels in 48 hours. Air conditioning and dehumidifying units enable both small and large polishing rooms to maintain uniform conditions throughout the year. This is a long step forward from the time that polishing rooms had to shut down for weeks because excessive humidity would not permit the animal glue to set, thus resulting in poor wheel life as well as performance.

Atmospheric conditions being uniform, other variables that affect drying conditions of animal glues are the density and thickness of film. This applies directly to the drying of the abrasive glue head and the density of the material forming the wheel face. In case of polishing wheels, thickness of the wheel head is the most important factor. Here, the strength of the glue, the abrasive grain size, and the number of coats applied determine the thickness of the head or the glue-abrasive layer. The thicker the head naturally the longer the drying time. It becomes evident from the foregoing that the glue solution will be thicker or thinner depending upon the type of work to be done by the polishing wheel. Plow shears may be used to illustrate this point. Wheels set up for this coarse work require more glue and more drying time than those set up to do fine grinding work. Both types may have the same number of coats, but whenever the grade or test of the glue is varied, the drying time will also vary accordingly.

Failure to dry the wheels properly may result in either underdrying or overdrying. Whenever the wheel is underdried, the glue head does not attain full strength. Such a wheel cuts slowly, inefficiently, glazes rapidly, and may even lose portions of the head while in operation; a dangerous condition. Overdrying, on the other hand, causes excessive brittleness and

failure of the glue to hold the grain. In such cases the grains will tear out of their sockets.

Finally, to test a wheel that is drying, hit it with a round steel bar and observe the readiness with which the glue film cracks. If it is still green or wet, it will not crack at all. If, on the other hand, the wheel is too dry, it will crack and splinter readily.

It is well to remember that the many characteristics of animal glues which have been discussed in some detail in the above application are more or less true for the behavior of animal glues when used in most other gluing applications. They should all be kept in mind when using hot animal glues as adhesives in order to obtain maximum bonding for the grade of glue used.

(d) *Paper Manufacture*

Since paper was first invented, its production and use have been closely associated with the use of animal glue. Beginning with the first step in the conversion of pulp to paper in the beater, and following the process through to the ultimate drying of the paper sheets, animal glue is intimately involved in most of the operations of paper manufacture. With the mechanization of paper production through such equipment as the Holland Beater and Fourdrinier "wet-ends", the applications of glues have found ever wider uses. Today their uses in paper manufacture can be divided into the following general types of application: beater sizing, surface sizing, machine coating and finishing operations.

A small percentage of animal glue is used in the beater for the purpose of surface sizing the fibers and also to serve as a colloidal flocculating agent in order to prevent the excessive loss of fibers and fillers through the effluent waters running out of the beater, the paper man's term for which is "white water". This is commonly brought about by maintaining the pH of the beater water at about 4.4 by addition of paper-maker's alum (aluminum sulfate).

A newer development employing this same principle is the SVEEN process. In 1927 a Norwegian, KARL SVEEN, was granted U.S. Patent 1,622,474 on a "Process of Effecting Agglomeration in Paper Pulp". Just before the paper pulp, mordanted with aluminum sulfate or some other mordant, passes on to the wire cloth, forming the incipient paper sheet or web, a small quantity of animal glue solution is added. A marked improvement is noted in the ability of the pulp to retain the filler and also in the recovery of the filler and fibrous material from the white water. The effectiveness of the glue for this purpose is said to be markedly improved if it is first aged for a few days at below normal room temperature.

The glue solution is prepared by dissolving one pound of glue in about 12 gallons of water. The pH is then adjusted with alum so as to fall between 4.2 and 4.4. According to the inventor, a coagulation takes place as a result of the reaction between the glue and the alum (aluminum sulfate) present in the pulp. This coagulation is characterized by "large, quickly-descending particles". LODDENGARD⁵ states that during the aging period the glue particles undergo a very marked change; the fresh hydrophile glue particles change to hydrophobe particles. It is claimed that the SVEEN process requires only $\frac{1}{3}$ of a pound of glue for each ton of finished paper.

After experimenting with gelatins, glues, starches, waxes and soaps in engine sizing, mill-men found more than one hundred years ago that rosin soap treated with alum in the engine sizing operation imparted water resistance to paper. Some paper makers add animal glue to the beater in conjunction with rosin size and find that paper so treated has many desirable qualities. Glue used in this way affords a protective colloid and is particularly useful in combating local difficulties with hard water caused either by natural conditions or by the use of fillers containing carbonates.

Again, in the manufacture of fine paper in which relatively small amounts of rosin sizing are used, the use of animal glue greatly improves the stock by encouraging the retention and dispersion of the rosin. Animal glue is also used in the making of hard finished boards and papers, body stock for coating, kraft for use in gummed papers, thin tissue for cable insulating or for spinning and twisting paper. Here the glue either imparts exceptional strength to the paper as in the case of gummed tape, or in the case of hard finished boards, eliminates surface fuzz without making the product brittle.

(i) *Paper Sizings*

In the manufacture of paper, the terms "tub sizing", "surface sizing", and "top sizing" are all used to refer to the process of applying gelatin, glue, or other sizing materials to paper that has been formed into sheets of a continuous web. Prior to the manufacture of paper in webs, it was the general practice to immerse the hand made sheets in a tub of animal glue or starch size. Hence the name "tub sizing" which has persisted to the present day. It is now used interchangeably with "surface sizing", the name commonly applied to the process of drawing the continuous web of a machine made paper through a sizing bath.

Many sizing experiments have been conducted by paper manufacturers as well as by the U.S. Bureau of Standards to determine the best materials or combinations of materials to be used. Tests have shown that glue tub

sizing renders paper relatively non-absorbent and gives it a smooth hard surface, the writing quality of which is superior to that obtained by the use of rosin alone. In addition, tub sized paper exhibits other desirable qualities such as firmness, resilience, and the ability to withstand repeated erasures. Strength and resistance to wear are also present in greater degree than when mixtures of starch or starch and animal glue were used.

Tub sizings are used in the manufacture of rag content bond and ledger papers. Certain photographic, blue printing, and special papers are also tub sized whenever permanency of record is especially desired. A recently expanding application is to be seen in the offset lithographic industry where greater efficiency in production results from the longer life which glue tub size imparts to the offset plates and blankets. Perhaps the most popular use of animal glue sizing is the dollar bill. Constantly subjected to creasing, folding, and crumpling, paper money must be able to withstand repeated handling. The Bureau of Engraving and Printing of the U.S. Government specifies sizing of all paper used in the manufacture of currency with animal glue. This sizing increases the folding endurance as well as the resistance to moisture, rubbing, and cracking of the bills.

(ii) *Paper Coatings*

Another important phase of paper manufacture and one in which animal glue is used for special effects is the production of coated papers. For instance, glue is commonly used in producing playing card stock, glazed papers, and other surfaced papers to meet unusual requirements.

Coated papers consumed in large part by the graphic arts industry and for packaging materials are prepared with mineral coatings. These are bound together and to the body of the sheet by a suitable adhesive, usually casein, soya protein, glue, or starch or a combination of two or more of the foregoing. The "coating mix" or "color mix" is prepared by suspending a mixture of mineral and adhesive in water and adding, in some cases, waxes, soaps, or similar softening or finishing agents.

Several factors may be involved in the selection of the proper adhesive for coating work such as adhesiveness, clay-suspending capacity, and water resistance.

Animal glue has a tensile strength of 10,000 to 12,000 pounds per square inch with the result that when the sealing wax pick test is conducted for this adhesive, the paper will be completely torn through. The clay-suspending capacities of glues do not always improve uniformly with increasing jelly test although they always increase or diminish with

like changes in the viscosity of the glue, as indicated by the sealing wax pick test.

Glue bound papers, used in certain processes such as those requiring repeated impressions of multicolor work, may be made more water resistant by the use of tanning or glue-hardening agents such as chrome alum, formaldehyde, or condensation products of the latter. Different grades of glue vary in their reactions to these materials. The higher grades require less of any tanning agent than do the lower grades in developing the same degree of water resistance.

While animal glue bound paper on the one hand permits the use of thinner and more fluid inks than does paper bound with substitutes, it can, on the other hand, give just as successful results with the heavier and more viscous inks.

(iii) Some New Applications of Glue-Sized Papers

By virtue of glue sizings and coatings, paper has found increasingly wider use by the graphic arts. One of the latest examples of the extension of the use of paper through the application of glue is paper furniture. Fibre reed furniture, made from strong twisted paper, is sized with animal glue. This protective coating imparts exceptional durability to the paper, and the same application is made use of for clothes hampers, baby carriages, waste paper baskets, etc. The paper gasket and the paper "can" also are in use today. Glue impregnated paper gaskets were used on large numbers of military engines for tank, car, and aircraft use to provide airtight and gasproof seals. This flexible, easily processed material is said to offer a tight seal, is easily removed, does not flux to metals and is more vibration proof than regular gasket materials. The paper "can" is equipped with a paper lining of plasticized glue and has been used successfully as a container for motor oils.

Still another war example of the successful glue-paper combination was the durable paper tube adopted as a shell container when condensation developed on the inside of metal shell containers in the humid atmosphere of the Pacific, resulting in corrosion of the shells. Paper tubes, joined with animal glue, served the purpose and kept the shells dry, clean, and free from corrosion.

(e) Woodworking

Few products can match the long and useful history of wood. One such product is animal glue. When used in conjunction with wood, animal glue

has created durable tools and weapons as well as household possessions for man for thousands of years.

Some of the desirable qualities of animal glue for woodworking are high tensile strength, free flowing consistency, quick set, non-staining action on wood, and adaptability to different use conditions.

With most woods animal glues are capable of creating bonds second to the strength of metals in terms of tensile strength. Properly prepared glue bonds are capable of withstanding stresses of 10,000 to 12,000 pounds per square inch. Since the shear strengths of most commercial woods is considerably less than the foregoing values, it is evident that there is a wide margin of safety to insure strong joint work. The attainment of such bonds, however, depends in large part on the technique of handling the glue and the preparation of the wood prior to gluing. Recommended concentrations for different grades of animal glues for use in woodworking are stated in Table 15.

TABLE 15
RECOMMENDED CONCENTRATIONS FOR ANIMAL GLUES IN WOODWORKING

Jelly test (see p. 153)	Parts of water by weight	Parts of dry glue by weight
120-150 grams	$1\frac{3}{8}$ to	1
150-175 "	$1\frac{1}{2}$ to	1
175-205 "	$1\frac{3}{4}$ to	1
205-235 "	$1\frac{7}{8}$ to	1
(2) 235-265 "	2 — to	1
265-296 "	$2\frac{1}{8}$ to	1
(1) 295-330 "	$2\frac{1}{4}$ to	1
330-360 "	$2\frac{3}{8}$ — to	1
360-395 "	$2\frac{1}{2}$ to	1
395-425 "	$2\frac{3}{8}$ -3 to	1

The actual viscosities in poises of a couple of the above mentioned glues designated as (1) and (2) at various concentrations, at 140° F are illustrated in Fig. 73.

In the foregoing discussion on "set-up" wheels, (see p. 163), the process of bonding was described in detail. It will be remembered that success in making a satisfactory bond with hot animal glue is dependent quite largely upon the consistency of the solution at the time of contact on the parts to be bonded. This condition applies especially to the use of animal glue in the bonding of wood. Although such factors as temperature of solution, temperature of the wood, temperature of the glue room, amount of glue spread, concentration of the glue solution, and assembly time all influence

greatly the consistency of the glue solution, the real underlying influences, however, are the jelling power and viscosity test of the glue itself.

When all of these variables are co-ordinated properly together with good machining of the wood and adequate pressure, maximum joint strength will result. The maximum percentage of wood failure will take place when ruptured (see Fig. 74 (1)).

Usually the greatest variations occur in temperature of the wood,

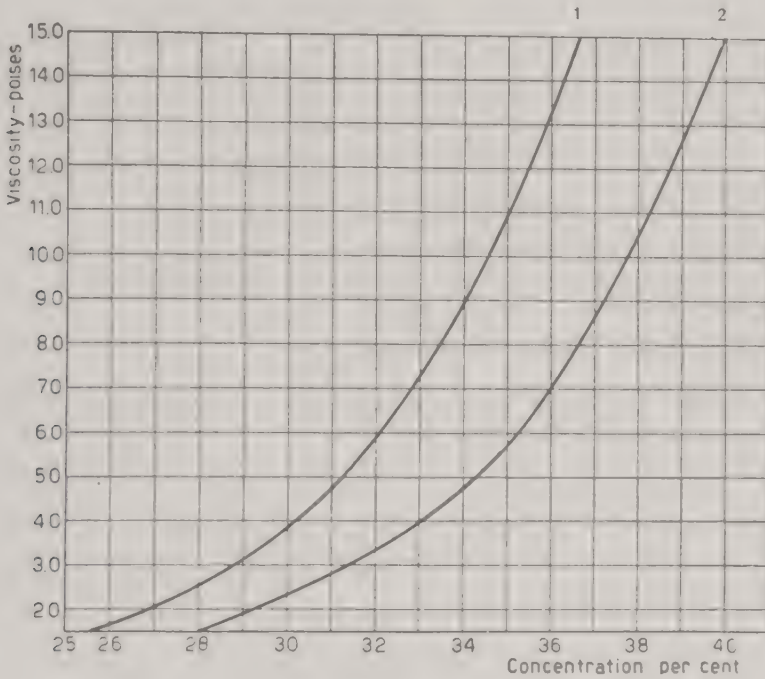


Fig. 73. Relationship between the viscosities of two commonly used woodworking glues at varying concentrations at 140° F.
Curve 1: 104 millipoise hide glue.
Curve 2: 85 millipoise hide glue.

temperature of the glue room, and the assembly time. These variations may be offset by compensatory adjustments in such easily controlled variables as concentration and temperature of solution. Occasionally, however, variations in technique occur without setting up the proper counterbalancing change. In such cases the result is one of three conditions representing poor gluing practice: a starved joint, a chilled joint, or a dried joint.

The starved joint (see Fig. 74 (2)) has insufficient glue in the joint, as the term suggests, and usually is caused by any one or a combination of the following factors: too high solution temperature, too thin solution, temperature of the wood too high, excessive pressure, or too short assembly time.

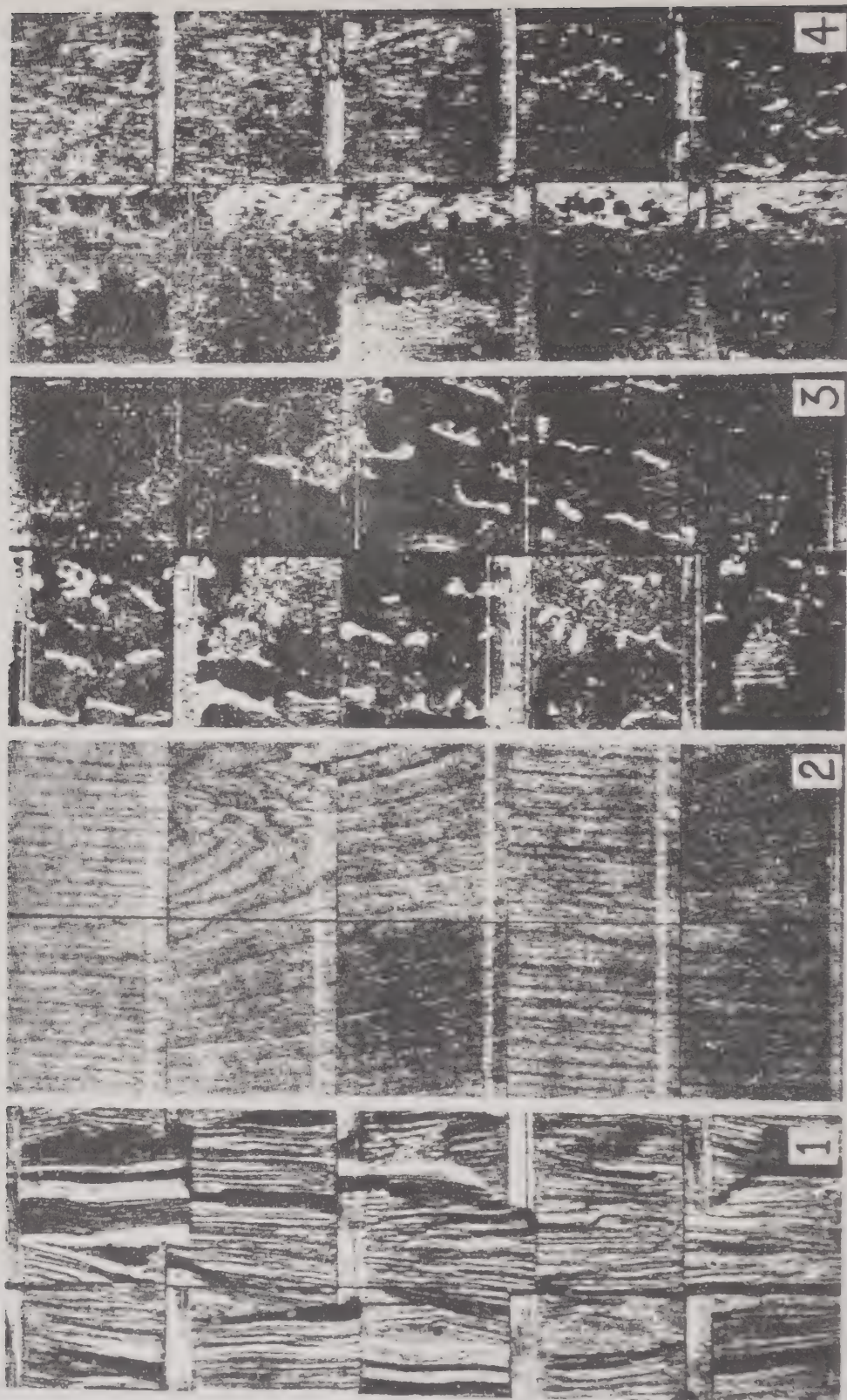


Fig. 74. Photograph of types of joints produced with animal glue under varying gluing conditions. (1) Well glued joint; (2) Starved joint; (3) Chilled joint; (4) Dried joint.

Courtesy of Forest Products Laboratory, Madison, Wis., U.S.A

The chilled joint (see Fig. 74 (3)) is often characterized by an excess of glue in the joint. Chilling of the glue before applying pressure precludes proper contact with the wood. In this case the condition is caused by one or a combination of the following variables: glue solution too heavy, solution too cool, wood too cool, too long assembly time, too thin glue spread, or insufficient pressure.

The third type of poor joint is the dried joint (see Fig. 74 (4)), one in which the glue film had dried before pressure was applied. The dried effect may also be the result of overheating the wood. Warm, dry wood promotes a rapid transfer of moisture from the glue film to the wood as well as evaporation into the atmosphere. Other factors, in the order of their importance, contributing to this condition are long assembly time, thin glue spread, and thin glue solutions.

Regardless of the type of poor gluing practice, corrective changes can be made readily and easily. As previously stated, the most commonly used corrective changes are proper adjustments in concentration and temperature of solution, especially the former. If further adjustments are necessary, consideration may be given to such factors as temperature of the wood, temperature of the glue room, glue spread, moisture content of the wood, assembly time, machining of joint area, pressure, and time in the clamps.

(f) *Textile Processing*

The art of rayon warp slashing or sizing can be said to have begun in 1919 when C. B. JOHNSON constructed the first multi-cylinder warp sizing machine. Previous attempts to size rayon warps on single drum cotton slashers were unsuccessful for quantity production.

With mechanical obstacles overcome, mill men were then able to turn attention to other problems, chiefly chemical in nature. Satisfactory trade acceptance of rayon textile fibers depended largely on the finding of a suitable sizing agent for protecting the delicate filaments during the weaving process. Natural fibers, possessing natural gums or oils for lubrication purposes, exhibit fairly high elasticity and strength. Synthetic yarns, devoid of these natural oils, require a protective coating of a size imparting great strength, elasticity, resilience and lubricating properties to permit proper processing.

The period between the two world wars witnessed the expansion of the rayon industry to its present production of more than one-half billion pounds yearly; it also witnessed almost universal acceptance of animal glue as the practical substance for use as a binder on filament rayon. Certain

waxes, starches, and linseed oil had also proved satisfactory in the slashing operation. However, it is necessary that any substance deposited on the yarn while sizing the warp be not permanently attached to the fibers. It must be capable of easy and economical removal by dyers and finishers.

In contrast to the use of enzymes, dissolving chemicals, or boiling, when starch size was previously used, the animal glue sizings merely require short soaking in cold water followed by melting in a jacketed kettle at moderate temperatures. Wide range of animal glues available, ease of mixing with plasticizers, stability, and ease of removal of the film on low temperature scouring were among other factors leading to the general acceptance of animal glue as the ideal sizing material.

In addition to its use in sizing the warp, animal glue is also used for crepe yarn soaking. In the finishing processes it provides a dye stabilizer, slip proof and splash proof silk hosiery. It can be used for weighting, ribbon finishing, and on nylon and vinyon yarns.

(i) Use in Sizing Rayon Yarns

Continuous filament rayon yarn has many filaments in parallel position. Size binds these filaments together and provides them with a flexible coating. Such a coating is not designed primarily to increase the strength of the yarn but to serve as protection against spreading filaments and abrasion during weaving. Size must not reduce the natural elongation of the yarn. If the size is not sufficiently flexible to stretch and contract to measurable limits, loom efficiency is reduced and substandard cloth will result.

Grades or types of animal glues used for this purpose will vary for the different deniers. Acetate rayon yarns are less water absorbent and require higher size concentration. Viscose rayon yarn is highly water absorbent and so offers little resistance to size penetration. Surface friction is reduced owing to its less static nature and so a lighter size coating can be used.

Most spun rayon yarns consist of short staple fibers, similar to cotton, and are spun on cotton machinery. Use of starch sizing presented difficulties inasmuch as either enzymes or boiling were needed to remove the starch. The former was expensive and the boiling tended to destroy the character of rayon.

Tests have indicated that a mixture of glue acting as a binder and soluble dextrin acting as a filler gave best results. The boil-off was skipped entirely, and desizing was done on the dye jig.

Taffeta, the easiest weave on the warp, requires the lowest size concentration to protect the yarn against abrasion. Satin weaves, on the other

hand, are more severe on the warp and require higher concentrations.

(ii) *Use in Rayon Throwing*

Glue plays an important role in the rayon throwing industry. Prior to twisting or spinning, the yarn is soaked in a glue solution. Hot water is absorbed and carried directly to the core of the yarn, thus insuring uniform contraction when the goods are subjected to the boil-off process of the dyer and finisher. It was quickly discovered that a low concentration of glue or gelatin would produce a long wave in the yarn and a high concentration would produce a short wave—hence the expression, coarse or fine pebble goods.

(iii) *Use in Finishes*

The main factor in any slashing solution is the balance of softener to glue. The greatest portion of animal glue used with textiles is used for rayon sizing. Its use as a stiffening agent in the finishing of textile fabrics is not so well known, since many cheaper sizes are available. Animal glue is recognized for its outstanding property as a protective colloid, particularly in preparation and stabilization of many water-repellent and splash-proof finishes currently available on the market. The low concentration of animal glue required to produce a stable, fine particle sized emulsion of waxes and/or metal soaps in this particular class of water repellent finishes permits greater economy in use and eliminates need for loading the finish with excess emulsifying agents. Properly controlled, the animal glue in such finishes may also serve as a water resistant size in its own right.

(iv) *Use as Dye Leveling Agent*

Again as a dye leveling agent, animal glue serves as a very effective protective colloid. The relatively small quantities of animal glue required to insure even take-up of the dye by the fabric permits great economy in use. The neutral chemical reaction of animal glue precludes any undesirable side reactions within the dye.

Careful surveys of specific mill requirements have recently made possible recommendations for the use of extenders with animal glue. The wide safety factor inherent in the sizing properties of animal glue has at times permitted a reduction in size requirements where extremely close plant sizing control is practised.

(g) Calcimine

Whenever one finds a high grade calcimine, the incorporation of a good grade of animal glue is evident. This close relationship exists since calcimine is basically a physical structure, held together with animal glue. The pigment is usually whiting, clay, marble dust, mica, and color. The animal glue binder is used to bind these materials together.

The outstanding property of animal glue, making it very suitable for use in calcimine, is its high binding power; that is, its property of bonding the powdery materials to themselves and then to fasten a film of the materials to a plaster surface. A high bonding power alone, however, would not qualify an adhesive for this purpose. Besides possessing high degrees of adhesiveness and strength, the adhesive must be available in the dry state. It must be powdered and of a density not too different from that of the finished product in order to prevent sifting or separation of the ingredients into layers while in transit. In addition to the foregoing qualities, the adhesive must be readily soluble under conditions of practical use on the job. The adhesive must disperse or spread completely through the solution in order that each inert particle of pigment is completely coated. At the same time it must supply the proper viscosity or body necessary for brush application so that the operator can spread the mix quickly and uniformly to a thin film on the surface.

After application, the adhesive must be able to dry into a continuous film, rather than become broken and collect in small droplets or globules.

All of these adhesive requirements set forth above as being necessary for use with calcimine are possessed by the proper grade of animal glue. The last requirement mentioned, namely, that of being able to dry in a continuous film, without migration, contributes probably the most to give calcimine very satisfactory permanency, permitting cleaning with wall cleaners.

Animal glue's ease of solubility from the dried film by warm water contributes greatly to the ease of removal of an old coating of calcimine, making it a simple operation when using a large sponge. The addition of a small amount of alkaline wall cleaner to the water will hasten the removal. The age of the calcimine film and its degree of dehydration will have no material effect on the ease with which the old calcimine may be washed off. In other words, calcimine is permanent as long as it is kept dry, but presents no problem when removal becomes necessary.

Through laboratory developments, animal glue manufacturers have produced calcimine type glues that are free of odor, sufficiently light in

color to prevent off-shades in the final product, free of natural animal greases, and also free of chemicals that might adversely influence such properties as spreading or color. Control of pH of the finished glues in the factory has contributed toward higher quality and better uniformity of glues for this particular purpose.

Two types of glues are used for calcimine, namely, a pure hide glue for use in a hot-water product, and a bone glue for use in a cold water product. Since the use of hot water is an absolute necessity with hide glue, the use of this adhesive is restricted to only those jobs where hot water is available. Bone glue, on the other hand, will develop full adhesive strength in warm water, or water which is not too cold.

The calcimine industry uses three or four different grades of each type of glue, hide and bone, in preparing different grades of calcimine. It is to be expected that the higher grade of glue used, the smaller is the amount necessary to produce a satisfactory calcimine coating.

§ 5. ADDITIONAL APPLICATIONS

Due to the limitations of space that must be observed in attempting to discuss in any detail so broad a subject as this one, it will be necessary to touch only briefly on a few more applications.

(a) *Composition Cork*

High grade hide glue is used as the binder for shredded or ground cork, in order to form it into sheet stock of desired thickness.

The glue solution is prepared, as previously described on p. 151, and then a predetermined amount of glycerin and hexamethylenetetramine are added just before the hot glue solution is added to the ground cork. This mixing is accomplished in a heated tumbler, in order that every particle of cork be coated with glue before the latter congeals.

The mix is then emptied into containers and aged in the open room for 24–48 hours. After this drying period the treated cork, still in a granular form, is fed to various types of machines which form it into sheets, blocks, or rods, according to end use. During this transformation the treated cork is subjected to heat and pressure at which time the previously dried glue layer melts, as a result of its glycerin content, and at the same time the hexa compound breaks down and gives off formaldehyde which insolubilizes the animal glue. The finished sheets may be used as a substitute for regular sheet cork. The rectangular blocks may be sliced into sheets which in turn

may be stamped into such items as gaskets, while the rods, about one inch in diameter, are sliced into wafers for use in beverage bottle caps, to effect a perfect seal.

(b) *Printers' Rollers*

The early discovery of the ability of a glue glycerin composition to carry and transfer printer's ink from the inking pad to the type was the sole reason for the early perfection of the first printing press.

Until comparatively recently, practically all printers' rollers were made from glue and glycerin. A high testing hide glue was used along with considerable glycerin. Formulations varied according to the type of work to be done. A comparatively small amount of water is incorporated, since the finished rolls must not give off nor absorb appreciable moisture, as this would result in a change in the dimensions of the roller.

With the invention of the high speed printing presses, the standard glue-glycerin rollers became unsatisfactory, as the generation of heat from the high speed machines would cause the all glue-glycerin rollers to melt down or become slightly off-center.

This difficulty was first corrected, temporarily, by insolubilizing the glue-glycerin rollers. Today, such presses use rubber rollers, usually coated on the surface with a thin glue-glycerin layer. This coating is used since no composition, to the writer's knowledge, has as yet proved as satisfactory for this particular purpose as the glue-glycerin composition.

Many combinations of rollers are used in the printing industry at the present time, however, the solid all glue-glycerin rollers are now found only on hand or slowly operated presses.

(c) *Photogelatin or Collotype **

Photogelatin or Collotype is a reproduction process representing one of our earliest applications of gelatin into this field. An outstanding characteristic of this type of printing is that the plate bears a very fine irregular screen, which originates from an almost invisible wrinkling of the gelatin surface.

This process is probably more commonly used in Europe than in America, since it represents a rather time consuming operation and one not suited to high speed production. Instead, it is commonly employed in the

* This represents a summary of an address delivered by WALTER FREDERICK, President of the Frederick Photogelatine Press, Inc., New York City, and THOMAS D. HOOK, Vice President and Sales Manager of the Black Box Photo & Collotype Studio, Inc., Chicago, Ill.

reproduction of such material as murals, oil paintings, water color prints, pencil sketches, architectural drawings and the like.

Preparation of the printing plate is somewhat similar to that used in offset printing. A formulation comprising gelatin, potassium bichromate, and ammonium bichromate is used to produce the plate coating. The proper technique of preparing the bichromate-gelatin solution is a direct function of the quality of the finished plate. A general procedure is to first put the gelatin in solution, then add the bichromates (in solution) and raise the temperature of the resulting mixture to 150° F. It is then advisable to clarify the solution before preparing the plate coatings. The latter are prepared on a vertical whirler and dried in an air current.

The light-sensitized photogelatin plate is then placed in a printing frame along with the mask or negative to be reproduced. Upon exposure to arc lights the light penetrates the gelatin coating thru the clear and translucent portions of the negative. The action of this light causes a hardening of the gelatin coating, varying in degree, according to the intensity of the light permitted to come thru the negative.

After the exposure has been completed, the plate is placed under running cold water. Here the unreacted, water-soluble bichromate salts are washed away from those areas of the plate which did not receive sufficient light to cause the bichromate to react with and harden the gelatin. Such unreacted areas of gelatin then naturally absorb some of the cold water and swell. Areas where light penetrated and caused a chemical reaction between gelatin and bichromate become hardened and as a result do not absorb as much water as the unaffected areas. This action of different degrees of swelling causes the surface of the plate to become somewhat irregular. The highlights of the negative are then represented by those portions of the plate with the least swelling or in other words, the depressions. Since the raised or swelled portions contain as much as 75% water, they have little affinity for the greasy ink, the latter being deposited to a greater extent in the depressions which will represent the shadows of the original negative. The balance of the image will accept the ink in direct proportion to the amount of light absorbed by the plate.

Before making the actual run, however, the plate must be hardened by using a mixture of water, glycerin, and formaldehyde. This toughens the gelatin to such a degree that it is possible to print up to 5000 or more impressions from one plate.

(d) *Bookbinding*

The use of animal glue in bookbinding may be compared to that just

discussed in the printers' rollers industry in that it no doubt played a major role in getting the early bookbinders started centuries earlier than they might otherwise have done.

The use of animal glue in this industry today has become so wide spread and complicated that it would be impossible to describe it accurately in anything less than a volume of its own.

As in the case of printers' rollers, and nearly every other application for that matter, the industrial cry today is for speed and more speed. The glue industry is being called upon to develop glues with faster and faster setting qualities, especially for use in the assembling of magazines where copies are now coming off the machines at a rate as high as 140 per minute.

In order to meet such demands, special glue compositions must be developed, embodying other ingredients such as plasticizers, tackifiers, etc. These compositions are usually furnished in cake form. They are melted down in the glue pot and usually no extra water is added. Many such combinations are used during the assembly operation of the book or magazine, each to perform a specific operation.

(e) *Manufacture of Toys*

Large quantities of animal glue are used in the toy industry. It has most of the characteristics which are necessary to the toy manufacturer such as mechanical properties, ease of preparation and application, and its ability to mix readily with such materials as sawdust, wood flour, abrasives, sand, clay, plaster, etc. It also has the property of being readily made flexible by means of a plasticizer. Its rate of set or gelation can be varied to suit needs or various operations. These qualities collectively have made animal glue quite a popular adhesive in this industry.

As a specific example, in the manufacture of dolls, the molded wood flour composition parts are bonded together with animal glue. The completed body or portions thereof are then dipped in a solution of animal glue containing zinc or titanium oxide, a plasticizer and the desired coloring.

(f) *Use of Glue in Matches*

Animal glue is the preferred adhesive for use in the manufacture of matches. It has been selected for this purpose due to the following reasons: ease of handling, jellying property, compatibility with and bonding together of the many ingredients comprising the match head, holding this mixture firmly onto the match stick, and last but not least, providing the proper

porosity within the match head in order to permit proper burning when struck.

Properly prepared animal glue for use in matches should be approximately neutral. However, if the glue being used does vary from neutrality, sufficient borax may be added to acid glues and an organic acid such as phosphoric may be added to alkaline glues to bring them to neutrality. It is the writer's opinion that glues so treated will not prove to be as satisfactory for use in matches as will glues which were produced with a neutral reaction.

Two special mixtures are used in match production. The first mix which is applied directly to the stick is known as the "base mix". A second mixture is applied to the tip of the "base mix" on the stick, and is known as the "tip mixture".

The "base mix" should be prepared by using a pure hide glue as the adhesive, testing in the middle range or about 225 to 250 grams Bloom test. This glue should be neither too foamy nor too foamless. The correct density of the mixture as required by most manufacturers is attained by mixing the proper proportions of a foamless glue with a foamy glue of about the same test.

The glue used in the "tip mixture", known as "tip glue", should be of a higher grade than that used in the "base mix". It should also be as free from grease as possible and have high foaming characteristics in order to produce a mix that will be much lighter than the base mix. It would then contain less protein per unit of volume. Such a glue should have a Bloom test in the range of 300 to 400 grams. When subjected to excessive agitation it should produce a stable foam comprised of tiny bubbles.

The purpose of the incorporation of air into the match head is to permit slow even burning. If a match pops, sputters, or explodes when struck, it is an indication that the composition of the head was too dense.

(g) Paint Cleaner

MACDONALD and STENGLE (U.S. Pat. 2,117,438) use 25–50% bone glue in a proprietary product known as "Spic and Span" for cleaning painted and varnished woodwork. Other ingredients comprise trisodium phosphate and sodium carbonate. The animal glue serves a two-fold purpose, namely, to emulsify the soiled film, thereby aiding its removal, and to provide a residue sizing which leaves a pleasing gloss on the washed surface.

H. HOLLANDER⁶ uses bone glue in floor polish. The glue is boiled for 12 hours, then soap, waxes, and white spirit are added.

§ 6. STATUS OF ANIMAL GLUE INDUSTRY AND PROSPECTS FOR THE FUTURE

Over the past decades the animal glue business has proved a barometer for general conditions, since its product is used by practically every industry.

From the standpoint of the glue manufacturer animal glue entered the post-war period in excellent shape. Factory inventories were at the lowest possible operating figures. No quick possibility of imports is apparent and production is expected to be maintained at current high levels in an effort to meet demands.

Almost all imports of glue by the United States in the past came from Europe. Several of the large European producing units have been put out of operation through bombings and removal of equipment. The pre-war level of European glue production will not be achieved again for some time because of lack of equipment and raw materials. This underproduction will be accomplished by an unprecedented demand. Millions of pounds of glue will be needed in rebuilding Europe's industries. American glue factories may have to supply a considerable portion of the requirements. The growth of animal glue production facilities in South America will do little to augment the overall glue supply. Raw materials, hitherto exported from South America to continental glue plants, will now be consumed by Argentina and Brazil glue plants. The increase in Latin American industrialization will provide a ready market for locally produced glues. Thus the demand for animal glue in the countries producing it will absorb the supply. In like fashion the United States will have to produce at home all of the glue required for domestic use. Thus, dislocation of European continental glue production and heavy glue demand by American industry promise to open up a period of intense activity for the domestic animal glue industry.

As animal glues flow into thousands of peacetime commodities, animal glue manufacturers plan large-scale programs centering on chemical and applied research. This program carries forward the trend of applying the scientific method to a natural product, and thus of widely increasing its usefulness.

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Figures 69 to 73 first appeared in a paper by Mr. L. B. LANE, Research Laboratories of Armour Glue Works, and the author, which was presented at the Fourteenth Midwest Regional Meeting of the American Chemical Society at Omaha, Nebraska in 1937.

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5 B. VEGETABLE ADHESIVES

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§ 1. INTRODUCTION

While by strict definition, the term vegetable glues could encompass such diverse adhesives as rubber cements and latices, nitrocellulose and ethyl cellulose lacquer cements, soya bean glues etc., the adhesive industry commonly designates as "vegetable glues" those adhesives manufactured by relatively simple processes from starch and from the water dispersible natural gums. It is appropriate to treat separately those adhesives which are applied from non-aqueous solution; and to include soya bean adhesives with other protein adhesives of animal origin.

Until quite recent years, certain starch adhesives had some application for the manufacture of cheap plywood, and may still enjoy a small market for packing-case plywood. For almost all durable goods these adhesives have been supplanted by synthetic adhesives which present the advantages of generally higher tensile strengths, better dimensional stability, moisture resistance and resistance to degradation by micro-organisms or enzymes.

Vegetable glues have, on the other hand, an increasing field of usefulness in the manufacture of non-durable goods, principally packing and packaging materials. Their relatively low cost, solubility in water and speed of adhesion recommend them highly for such purposes. Most of the high speed packaging machines and bag and carton making machines are designed for, and depend on the use of, vegetable glues.

Vegetable glues may be classified thus (arbitrarily excluding vegetables. proteins):

I Starch based adhesives

A. Dextrines

- (1) White dextrines
- (2) Canary dextrines
- (3) British gums

B. Acid hydrolyzed starches

C. Enzyme degraded starches

D. Oxidized starches

E. Gelled starches

- (1) Alkali gels
- (2) Salt gels

F. Water soluble starch derivatives

II Water soluble cellulose derivatives

III Natural gums.

Much of the foregoing nomenclature is arbitrary, and the classification is incomplete and too rigid. It will however serve as a framework for discussion.

§ 2. STARCHES

Starch is a polysaccharide of high molecular weight. The molecular weights of undegraded native starches are perhaps less accurately estimated than the molecular weights of native celluloses. Numerous estimates indicate that the average D.P. of starch is of the order of 1000. The greater complexity and greater fragility of the starch molecule make such measurements more difficult.

It is generally considered that starch has two constituents, designated respectively as amylose and amylopectin. Amylose is visualized as a straight chain, or almost straight chain structure of glycopyranose rings bonded in the 1 and 4 positions. Amylopectin, on the other hand, is visualized as a highly branched structure, bonded in the 1,4 positions mainly but

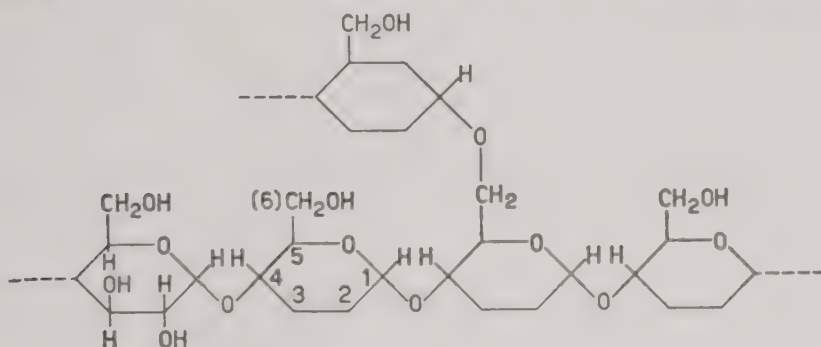


Fig. 75. Schematic structure of amylopectin molecule.

with branches originating (Fig. 75), more or less randomly, from the 6 positions ^{1, 2, 3}. Amylose fractions show a D.P. of 200 to 600; amylopectin of 1500 to 1800.

Starches are frequently described as containing stated proportions of amylose and amylopectin. Such values however are only meaningful if the method of differentiation is reported. Numerous determinations have been based on a series of extractions of whole starch granules with water, each successive extraction being at a slightly increased temperature, until the temperature of gelation of the starch is almost reached. The combined water extracts are considered to contain the amylose fraction; the extracted granules, the amylopectin. These fractions have markedly dif-

ferent characteristics ⁴. Fractional precipitation with butanol or a similar solvent also effects the separation of amylose and amylopectin ⁵.

Amylose displays marked crystallinity. Its water dispersions pass rather quickly from a viscous to a plastic state or to a gel. These phenomena, ascribable in the first case to the formation of crystalline aggregates of quite linear molecules, and in the second to the more random action of intermolecular forces, are collectively referred to in the adhesive industry as "pasting back", "setting back" or "reverting".

Amylopectin, on the other hand, when dispersed in water by means of heat or chemical agents, will retain its predominantly viscous characteristics for long periods.

Thus, when it is said that a corn starch based adhesive tends to set-back, it may be understood to reflect the relatively high content of amylose-like molecules in the starch.

Amylose and amylopectin should not be regarded as absolute terms. Not only do the relative proportions vary by definition according to the method of estimation used, but, keeping the method constant, considerable variation is found between samples of starches from a given plant species and even between immature and mature granules from a single planting. Since it is apparent that scission of short straight chains from the amylopectin molecule can occur during acid hydrolysis ⁶, it is not improbable that some part of the amylose fraction may have resided in the amylopectin of the native starch.

Bearing in mind the indistinctness of the terms, it can be said that grain starches are generally high in amylose; root, stem and tuber starches are high in amylopectin. Even this statement is open to disagreement. Rice starch and the recently much discussed waxy maize starch provide adhesives with relatively little tendency to set-back.

The starches most commonly used in adhesive manufacture are tapioca, sago, corn, white potato and more recently, waxy maize and sweet potato. The adhesive manufacturer prefers a mature starch, undegraded by auto-genous enzymes, low in ash and protein. For enzyme conversions of starch to adhesives, a low phosphorus content may be desirable. For the manufacture of most adhesives, particularly dextrans and alkali conversions, uniformity is important and the manufacturer prefers to buy in lots as large as practicable, so that conversion procedures can be standardized over a reasonable period. Industrial starches are more commonly controlled according to the seller's specifications than according to the purchaser's. Some adhesive producers have established limited purchase specifications, based on ash, protein nitrogen, viscosity of alkali dispersions or the like.

Tapioca starch has been favored in the United States for the manufacture of envelope and postage stamp gums, remoistening gums for tapes and labels and for many other high grade dextrine applications. White potato starch achieved popularity in Germany for these same uses, but dextrines made from it have had the drawback, for remoistening gums, of a pronounced bitter taste. Sago starch has largely been used for the making of so called alkali conversions. Sweet potato starch which was initially developed in the United States with government subsidization, has gained some acceptance in spite of economic difficulties inherent in a short producing season and technical difficulties due to its dark color. Corn starch is very widely used in the United States as a raw material for all types of adhesives. Being produced by responsible and technically competent companies, a variety of closely standardized corn starches has been available at attractive prices, and a large formulary of adhesives has been built on these. Waxy maize is a newcomer to the adhesives field within the last decade. Its excellent adhesive characteristics have justified steadily increasing acreages. Rice starch and wheat starch are rarely used for adhesives.

§ 3. DEXTRINES

The term "dextrines" as used in the adhesive industry covers only the products obtained by roasting starch with or without chemical reagents. It excludes starches or starch fractions degraded by other means.

Dextrines are commonly classified as "white dextrines", "canary dextrines" or "British gums". A white dextrine is one which has been roasted in the presence or absence of acid or acid forming substance to a point short of complete solubility in cold water. Canary dextrines are those which have been roasted with an acid to complete cold water solubility, and then for an additional period during which the dextrine gradually darkens until its solution in water ranges from a light to a dark amber. British gums are roasted to complete solubility without acid, and generally for an additional period as well. The roasting periods are usually longer and the colors very much darker.

The acids used as adjuncts to dextrinizing are usually hydrochloric or nitric. Non-volatile acids such as sulfuric and phosphoric have been found unsatisfactory. Acetic acid has been used as a diluent for hydrochloric acid. Ammonium bifluoride is occasionally used.

While some oxidation may take place when nitric acid is employed, the function of the acid generally is simply hydrolytic, and the degradation of the starch is not an inherent part of the dextrinization process. Actually

the acid (which is diluted, sprayed into the starch and well dispersed by mixing, prior to the roasting operation) is largely lost, together with the moisture of the starch (11% or more, initially) in the first fifteen minutes or so of heating, while the heating may be continued for a number of hours.

An "acid converted dextrine" may be considered to be an acid degraded starch, subsequently dextrinized. The quantity of acid used controls the viscosity of the product. Time and temperature of roasting control other characteristics, to be discussed.

The molecular weights of dextrines are much lower than of the starches. The average molecular weight of British gum has been stated to approximate 15,000 with only a small fraction of lower molecular weight material. Canary dextrines show wider molecular weight distribution with fractions ranging down to the simple sugars. White dextrines, which may vary in cold water solubility from almost 0% to almost 100%, may vary correspondingly in their molecular weight characteristics.

While the starches have claimed the attention of numerous competent investigators, very little precise work has been done on the dextrines of commerce. Their constitution is indeed in considerable doubt.

Dextrines from corn starches show the characteristics designated as amylose-like; those from tapioca starches are amylopectin like. That is, corn dextrines unless particularly modified will in water solution become plastic or "pasty" more or less rapidly, while tapioca dextrine solutions retain their viscous characteristics. It is not unreasonable then to assume, until experimental evidence clarifies the situation, that dextrines derived from highly branched amylopectin retain that general configuration, even when acid hydrolysis has accompanied the dextrinization.

It has been proposed that dehydration of glucopyranose units may occur during dextrinization, with the formation of inner ethers, *i.e.* by etherification of the hydroxyl group on C atom 1 with that on C atom 6. Cross linking between chains is also hypothesized^{7, 8}.

§ 4. DEXTRINE ADHESIVES

Adhesives prepared from heat converted dextrines, with or without concomitant acid degradation, are by far the most important of the starch based adhesives for industrial use. They may be used in water solution without further alteration or may be further converted by other processes or modified by the addition of other substances. The variety of modifications and adaptations can be better exemplified than presented in detail.

The partly soluble white dextrines are almost always subjected to

additional treatment before use. By heating suspensions of such dextrans to a temperature above about 70° C, they are completely "dissolved". Granules only slightly different from the original starch are bursted. The solutions thus formed display elastic, plastic and viscous characteristics, dependent on the characteristics of the dextrin and of the original starch.

Alkali modification of these solutions produces a type of adhesive widely used for applications where a fast setting, low cost adhesive which will not permeate porous papers is needed. The manufacture of paste-boards is such a use.

Strong alkali—usually sodium hydroxide—suppresses the elastic properties and provides a viscous liquid glue which (again dependent upon the extent of conversion of the dextrin) may be mechanically spread in thin films at total solids concentrations ranging from about 25% up to 65% or 70%.

Various salts are used in combination with dextrans. Sodium tetraborate, trisodium phosphate and the acid phosphates, sodium carbonate, sodium silicate, sodium nitrate and others are used to effect desired changes in viscosity, pH, drying rate or adhesion to various surfaces. Calcium chloride and calcium nitrate are occasionally used to retard drying or provide hygroscopic films.

Dextrin adhesives are frequently plasticized with glucose or sucrose, glycerin, diethylene glycol or sorbitol. They may be reduced in viscosity by additions of urea, formamide or acetamide. Simple substituted amides such as dimethyl formamide have a pronounced solvating and thinning action on dextrin solutions.

Plasticizing of dextrin adhesives has been accomplished with such salts of organic acids as sodium lactate and sodium tartrate. Organic acids are frequently added to dextrin adhesives particularly for improving adhesion to envelope "bond" and similar hard papers. Citric, lactic, tartaric and hydroxyacetic acids have been used or proposed for use for this purpose. Occasionally inorganic acids in small quantity are added. Non-volatile amines such as triethanolamine have been proposed for use in dextrin adhesives, as have the strong quaternary ammonium bases. It is probable that cost considerations have limited the use of these to the present time.

Water miscible organic solvents may be used to alter the wetting or penetration characteristics of dextrin adhesives or even to hasten the drying rate. The simple alcohols, cellosolve and methyl cellosolve, dioxan and diacetone alcohol have been used not infrequently for particular purposes.

Sodium tetraborate, "borax", is one of the most widely used modifiers

for dextrine adhesives. It and some other salts (such as sodium stannate) affect solutions of British gums and white dextrans in such a way as to apparently increase their speed of adhesion.

A solution of British gum in water at, say, 25% solids will, when spread in a thin film, increase slowly in viscosity as water is lost by evaporation. It may retain its fluid characteristics until it has reached, for example, a solids concentration of 60% at which concentration it ceases to flow and assumes the characteristics of a gel. When this transition occurs it can be said that adhesion in a practical sense has taken place. Further loss of water by the film results in the development of tensions. If the film has been spread on glass or metal, it may break cleanly away or may develop cracks or fissures. If it is spread on a paper or other flexible surface the film will curl inward as it dries and shrinks. The addition of borax to such a British gum solution has the effect of causing the transition from a viscous state to a gel state to occur at a lower solids concentration. Initially formulated with 25% solids the adhesive may with the addition of 1% or 2% of borax lose its fluid characteristics at 45% solids rather than 60%.

Much of the modern high speed machinery used for the fabrication of cartons, bags and wrappers depends for the successful forming of the article on the use of an adhesive having a fast "set". For speed of operation in many applications it is therefore desirable to advance the transition point. Similarly in bonding of very porous papers, textiles or other permeable surfaces, advancing the transition point limits the penetration of adhesive. In addition it is frequently possible to use less concentrated adhesives and achieve better economy by this means.

As it has been noted however, after the fluid characteristics of the adhesive have been lost the film shrinks on further drying. When relatively rigid elements are to be bonded such shrinkage may do no harm and may even have the effect of increasing the strength of the adhesion. On the other hand when light weight papers are bonded excessive shrinkage of the drying adhesive film will probably result in warping or curling. The use of such agents as borax must then be practiced with some care.

White dextrans and canary dextrans roasted with relatively small amounts of acid, so that hydrolytic degradation has not been extensive, behave with borax similarly to the British gum exemplified above. A highly degraded canary dextrine displays the effect to a much smaller degree.

Dextrans used for the manufacture of envelopes, display cards, and similar articles where warping or curling would be highly detrimental are commonly formulated in water solutions at a quite high solids concentration. They are commonly canary dextrans prepared from tapioca starch

or waxy maize starch and so processed as to have as narrow a molecular weight distribution as possible. Dextrinization must be continued long enough to assure against the presence of any cold water insoluble starchy fraction which will cause the film to shrink and warp during the later stages of drying. On the other hand acid hydrolysis must not have been allowed to proceed so far as to produce simple sugars and other low molecular weight fractions which retard the ultimate drying of the film and are sufficiently hygroscopic to become tacky at high humidities, thus perhaps causing bundles of envelopes to seal shut.

A true plasticizer for dextrines has been sought by the adhesive industry, which would welcome the advent of a substance which by simple addition to dextrine adhesives would render their films flexible, non-cracking and less susceptible to dimensional changes with changes in humidity. In general humectants accomplish these purposes simply by causing the film to reach equilibrium with the ambient humidity at a higher moisture level. This however has the undesirable effect of promoting blocking as noted above and demonstrates that water is a good plasticizer for dextrines. Water is similarly a good plasticizer for cellulose and since no other effective plasticizer for cellulose has been proposed to date it seems unlikely that an additive will be discovered to meet all of the requirements of the adhesive industry.

As with cellulose however, substitution of replaceable hydrogen at intervals along the dextrine chain may serve the desired purpose. The mild acetylation of dextrine will provide films of greater dimensional stability together with other desirable characteristics.

The canary dextrines and the British gums which are said to be roasted to complete solubility form water solutions which are essentially viscous in character especially if solution has been accompanied by heating to 85°C or higher, which has the effect of completing the gelation and dispersion of the higher molecular weight fraction. All such solutions will have some plastic characteristics however, *i.e.*, measurable yield points. Plastic characteristics may be reduced in a number of ways. The inclusion of a small amount of sodium hydroxide or other alkaline material while "cooking up" the dextrine solution causes more complete gelation of the starchy fraction than can be accomplished by heat alone. The alkali may be neutralized subsequently without causing a regain in plasticity. Various additives to the finished adhesive solution will also reduce plasticity. Sodium chloride and sodium nitrate are moderately effective. Urea has a pronounced effect. Formaldehyde in relatively small amounts is useful. Dioxane is unexpectedly useful for this purpose.

The white dextrines provide solutions of higher plasticity. Those which are only partially soluble in cold water, that is, which are relatively starch-like, are often used for the preparation of "pasty" adhesives where plastic properties are desired for particular machining requirements. Such low soluble white dextrines are in fact converted into viscous liquid adhesives only by additional conversion procedures or by formulating with considerable quantities of borax or other alkaline material. Plastic properties of pastes are controlled by the blending of high and low soluble white dextrines and by formulating. Colloidal clays, sulfonated tallow, urea and a variety of inorganic salts are frequently used. In certain machine operations the viscous liquid dextrine adhesives show the property of stringing or cottoning. The effect is particularly likely to be encountered when the adhesive has been so formulated as to give a steep viscosity slope, *i.e.*, a rapid increase in viscosity with increase of solids. The effect is frequently combated by adding to the dextrine a minute amount of undegraded starch or high molecular weight dextrine fraction or by adding a material which in the dextrine solution is only slightly compatible. Gum tragacanth and other natural gums have been used. Carboxymethyl cellulose, polyacrylic acid and polymethacrylic acid show similar effects. The action of these substances is not well understood. It has been argued that conferring slightly elastic properties on the solution results in the breaking of thread-like filaments before they have lost moisture by evaporation. It has also been suggested that minute gel like particles of incompatible material cause discontinuity in the filament structure which causes breaking as soon as the filament has been drawn to a diameter approximating that of the dispersed particle.

The inclusion in the adhesive of a water miscible solvent which is not a solvent for dextrine and which has a vapor pressure less than that of water also tends to minimize or eliminate stringing perhaps by causing precipitation of dextrine particles in the drying filament.

§ 5. ALKALI CONVERSIONS

The temperature of gelation of starch and water is very much reduced by sodium hydroxide or other alkalis. Gelation is also more complete in the presence of alkali and the resulting starch dispersion is less gelatinous and more viscous than if accomplished by heat alone.

One of the methods used for the direct conversion of starch into useful adhesives comprises treatment of the starch suspension with sodium hydroxide. Sufficient quantities of alkali are used usually that the conversion

in its initial stages can be accomplished at room temperature or even below.

Such adhesives are usually manufactured in tanks equipped with heavy duty agitators which provide a rather complex agitation pattern such as the planetary type. As sodium hydroxide is added to the starch suspension a highly gelatinous mass is at first produced. As efficient agitation is continued this breaks down to a more viscous consistency. The gel or elastic characteristics are not wholly lost however and at end of the operation the adhesive may have a consistency characterized as "ropy".

Such adhesives are frequently used without further modification where an adhesive of moderate water resistance is required. Dried films of such adhesives are, as would be expected, hydrophilic but they can absorb very large amounts of water without losing homogeneity; that is they become gummy but do not readily disperse.

Various modifications of these adhesives are employed. Tapioca and sago starches are most commonly used; potato starch occasionally. In their simplest form they can be thought of as starch molecules to which sodium ions are strongly bound. Partial neutralization of these compositions quickly alters their ropy consistency to a plastic one and a variety of soft pastes can be made in this way.

The products are frequently treated with oxidizing agents during the agitation period, sodium peroxide or hydrogen peroxide being generally used. Alkali starch like alkali cellulose is not subject to hydrolytic degradation unless some oxidation intervenes. Wherever oxidation of the starch chain has taken place however there is possibility of alkaline hydrolysis with the result that in such treatments the viscosity of the solution is slowly reduced to provide viscous liquid adhesives. The dried films from these are considerably less resistant to water. Nitric acid is also sometimes used for these oxidations, partial neutralization being accomplished during the oxidation period.

The viscosity of these adhesives is greatly augmented by addition of borax or more particularly sodium stannate. The addition of more than about 0.01 % of sodium stannate will actually coagulate the mass.

In the United States adhesives of this general type have been extensively used for low cost veneer glue and for bottle labeling where it was desired that the label be moderately resistant to removal by cold water.

§ 6. SALT CONVERSIONS

An adhesive of soft pasty consistency, slow drying and moderately hygroscopic, is made by the so-called salt conversion. Like the alkalies a number

of inorganic salts have the property of reducing the gelation temperature of starches (a few salts have the reverse effect). Zinc chloride, magnesium chloride, calcium chloride and calcium nitrate are frequently used for this purpose.

Tapioca starch is frequently used for salt conversions. White dextrines are sometimes used in place of or as an adjunct to starch in order to increase total solids without passing through a period of excessively high plasticity which would overload agitators. The starch or dextrine slurried into water is treated with as much as 15% of the converting salt and heated quite slowly to avoid too rapid gelation.

Adhesives of this class are variously modified to confer special properties; by the addition of urea, other hygroscopic materials such as glycerine or sorbitol, by the addition of fillers, acids or alkalis.

The mounting of display samples on pasteboard and similar uses where warping of the adhered elements would be detrimental, provides the principal market for these adhesives. The adhesives are soft "buttery" pastes, are moderately thixotropic and are exceedingly slow drying.

§ 7. ENZYME CONVERSIONS

The method of degrading starch by malt enzymes has been employed by the adhesive industry for many years. Until recent years the malt enzyme preparations available in commerce comprised a mixture of alpha and beta amylase and were not always sufficiently well standardized to give uniform performance. Alpha amylase prepared from *Bacillus mesentericus* is a well standardized commodity and is now in general use.

The difference in behavior of alpha and beta amylase are extensively discussed in the literature⁹. In brief summary it may be said that alpha amylase attacks the starch molecule as a whole. Presumably it is able to attack the polysaccharide chains anywhere along their length to produce molecular fragments of irregular size which may then be further ruptured to produce ultimately glucose, maltose and simple low molecular weight dextrines. Alpha amylase attacks both amylose and amylopectin readily and no clear cut terminal point of the reaction is discernible. Alpha amylase is readily destroyed by acidifying the substrate to a pH of about 3.0.

Beta amylase apparently does not attack the starch chains laterally but erodes the chain terminals splitting off successive molecules of maltose. The action of beta amylase on amylose is continuous, the reaction proceeding slowly but uniformly until the chain is completely hydrolyzed. Beta amylase has relatively little action of amylopectin. The

situation suggests that the reaction is stopped at chain junctions so that the highly branched amylopectin can be "pruned" down only as far as the outermost branchings (Fig. 76.) Beta amylase is readily destroyed by heating to 70° or 75° C.

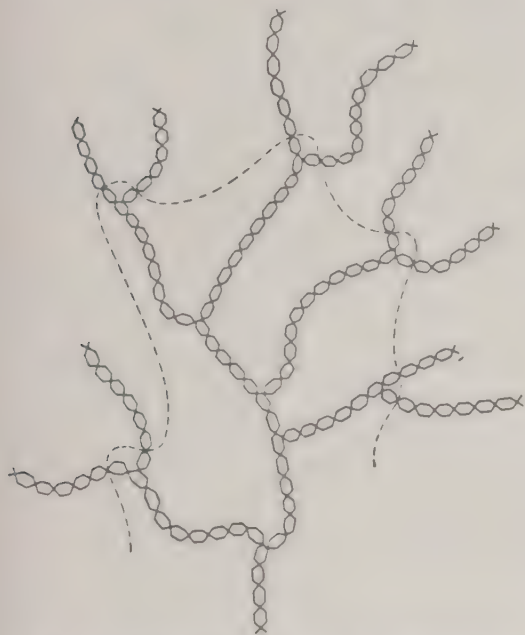


Fig. 76. Amylopectin: limit of degradation by beta amylase.

Until quite recently the industry did not consider it practicable to carry out enzyme conversions at high initial starch concentrations. The conversions are carried out at temperature high enough to initiate the gelation of the starch and, at the same time, they must proceed for a considerable period before extensive liquefaction takes place. In consequence high starch concentrations present a problem in heavy duty agitation.

Various means have been taken to overcome this. Mixtures of starch

and white dextrine may be used as the starting point of the conversion. A starch oxidized by initial treatment with chlorine or with a peroxide may be used. The addition of moderate quantities of urea at the beginning of the operation will reduce the rate of increase of viscosity with temperature and will not adversely affect the action of the enzyme. When unmodified tapioca or corn starch is used the initial starch concentration cannot exceed about 15%. The enzyme degraded product therefore must be concentrated by one means or another. Some producers have concentrated the product by evaporation. One manufacturer formerly used the expedient of converting initially at 15% solids then repeating the conversion with successive small additions of starch. This of course had the undesirable effect of widening the molecular weight range of a product which at best is a highly heterogeneous composition ranging from starch-like fragments to simple sugars. One manufacturer is said to have used the procedure of inoculating a finished enzyme conversion with yeast to remove the sugars by fermentation.

The conversion of starch by beta amylase is accomplished by raising the temperature of the starch suspension to 55° C and then increasing the temperature very slowly through the range at which the enzyme is most active to 68° C. The process is controlled by removing samples at frequent

intervals for determination of viscosity; retarding or accelerating the rate of heating and possibly adding additional enzyme until the desired viscosity is reached, when the batch is quickly heated to 75° or higher to destroy the residual enzyme.

The physical characteristics of enzyme conversion products are peculiar. If cooled and stored without further agitation they will commonly set up to rather stiff paste. These pastes display a characteristic which is commonly but erroneously called thixotropic. On vigorous agitation they break down to a viscous liquid state which shows relatively little plastic behavior. On standing they again revert to a pasty consistency. Each time that such agitation is performed the reversion to a pasty state is slower. Ultimately the products will remain fluid almost indefinitely. By the same token if an enzyme converted product is stirred continuously during the cooling period, its reversion to a pasty consistency is much retarded.

Since for many mechanical applications such a change in physical state during use is undesirable, enzyme conversions are sometimes modified by addition of, for instance, a white corn dextrine which will confer irreversible pastiness on the product.

§ 8. STARCH AND CELLULOSE DERIVATIVES

Two water soluble cellulose derivatives are currently available; methyl cellulose and the sodium salt of carboxymethyl cellulose. These are finding various applications in the adhesive field. Beta hydroxyethyl cellulose is soluble in aqueous solutions of mild alkalies and may have found some applications. Highly degraded cellulose acetate is water dispersible but has not to date been available for development by the adhesive industry.

Corresponding starch derivatives, while presenting no serious difficulties of manufacture, are not available in large quantity.

In addition to the branched chain structure of amylopectin which imposes a considerable randomness on the starch molecule, amylose chains are considerably more kinked than cellulose chains, consisting as they do of glucopyranose units united through carbon atoms 1 and 4 in an alpha-alpha-alpha-alpha configuration rather than the alpha-beta-alpha-beta configuration of cellulose. Thus starch cannot form the compact unit cell characteristic of cellulose and is more readily hydrated and dispersed in water. It follows that the starch derivatives are more readily dispersible in water than corresponding cellulose derivatives of the same polymeric degree.

Since amylopectin after being freed from the starch granule is relatively

cold water soluble and amylose, even after it has been allowed to form crystallites, is hot water dispersible, it is evident that substitution to a very minor extent, say by methylation or carboxymethylation, will provide very readily water dispersible derivatives. The acetylation of 1.0 or 1.25 hydroxyl groups per glucose residue yields products which are rapidly soluble in cold water and form optically clear solutions.

If, in the course of the reaction considerable degradation of the starch has been permitted to occur, the solutions are of the expected low viscosity and can be successfully used as high solids concentration solutions in mechanical equipment and for uses which would ordinarily employ dextrans. The dried films from such products are in general less hygroscopic than dextran films and may be used as envelope seal gums, for remoistening tapes and for similar purposes under conditions of humidity which would prohibit the use of dextrans. Probably for reasons of steric hindrance these products show little tendency to pass through a gel stage during drying. Where dextrans may shrink and cause curl or warp during the latter stages of drying these water soluble derivative films develop little tension.

These films are also considerably more flexible than dextrans. They have good remoistening characteristics except that over-wetting may dissolve and displace the film. They have been proposed for use as envelope and postage stamp gums in admixture with ordinary dextrans to provide a flatter more flexible film but one less sensitive to removal by solution.

If substitution of the starch is accomplished without extensive hydrolytic degradation the resulting high viscosity products have fewer adhesive applications. As one of a very few possible examples, the leaf wrapping of cigars employs a low solid content high viscosity adhesive of the type which these would provide. Gum tragacanth has been employed for this use in the past and is now being supplanted by water soluble cellulose derivatives such as sodium salt of carboxymethyl cellulose.

§ 9. NATURAL GUMS

Trade terminology employs "gum" to cover a variety of water soluble high polymers, gum arabic, gum tragacanth and the like, and also a large number of natural resins, gum elemi, manila gum, gum zanzibar, gum chicle, etc. Although this latter class of substances derives from vegetable sources it is appropriate to consider them elsewhere since in their adhesive applications they are used in non-aqueous solution, frequently in combination with nitrocellulose or other cellulose derivative, and since in any case they are as adhesives principally of historical interest, being displaced by synthetic resin formulations.

Gum arabic is perhaps the most widely used of the water soluble natural gums. As a polyglycuronic acid its properties are subject to variation by the nature of the combining cations. Potassium, magnesium and calcium are present in varying proportions in the natural gum. Variations in viscosity of solutions dependent on differences in polymeric degree provide another source of variation.

Since the industrial applications for gum arabic adhesives are quite limited, not much work has been done to control its physical characteristics precisely. It is generally used in water solution containing also some glycerin, sorbitol or other humectant to retard drying and to soften the dried film. Such a solution wets and adheres to some surfaces more effectively than the dextrine adhesives. Adhesives for smooth hard surfaced glassine papers are frequently based on gum arabic. Adhesives for bonding aluminum foil to paper have in the past comprised gum arabic solutions modified with a small amount of tartaric or a similar acid. Such adhesives must be used with caution since they may corrode aluminum foil to a damaging extent. Gum arabic solutions are occasionally used as remoistening gums especially for very light weight papers, since the drying film shows little tendency to curl.

Gum tragacanth and several other water soluble gums whose aqueous solutions display relatively high viscosities have a few adhesive applications which are now being taken over by the water soluble cellulose derivatives. The wrapping of cigars and the temporary bonding of hides to stretching boards have employed gum tragacanth. Almost equally important perhaps has been the use of this gum to modify the properties of adhesive emulsions which are almost invariably of the oil in water type. Increasing the viscosity of the external phase, of course, affects the gross properties of the emulsion to an important degree and usually tends to stabilize the emulsion. In very low concentrations however, from 0.001 to about 0.01% gum tragacanth and other viscosity increasing agents will promote creaming of rubber latex and other fine particle emulsions and dispersions by inhibiting Brownian motion.

§ 10. ACID HYDROLYZED STARCHES

An important class of industrial adhesives are prepared by the controlled hydrolysis of starch with strong mineral acids. The preparation of such adhesives frequently comprises the suspension of starch in water with addition of the acid at a temperature below the gel point and employing a controlled rate of heating, so that reduction in viscosity resulting from

degradation counteracts increase of viscosity due to gelation. The procedure is controlled by means of periodic sampling and viscosity determination. The acid is neutralized with a predetermined quantity of caustic when the desired viscosity has been reached. Skillful manipulation is required since the rate of change of viscosity is rapid and since the physical characteristics of the finished adhesive will vary considerably with small differences in viscosity at the time of neutralization.

These adhesives if simply neutralized are generally strongly plastic, *i.e.* ranging from stiff to soft pastes dependent upon the extent of hydrolysis. The addition of further quantities of sodium hydroxide or other alkalies converts them into viscous liquid adhesives similar in their applications to the alkaline dextrine adhesives.

These so-called acid conversions are also frequently further modified by oxidation with peroxides or by the addition of inorganic salts, urea, sugars, etc. Variations are also produced by modifying the original starch with some preformed dextrine, usually a white corn dextrine.

§ 11. STARCH OXIDATIONS

Adhesives of some industrial importance may be produced by the oxidation of starch with hydrogen peroxide or with hypochlorites.

Starches are frequently modified by hypochlorite treatment without rupture of the starch granule, simply by suspending the starch in water and treating with hypochlorites or chlorine under controlled conditions of pH and temperature. The resulting products, often misleadingly called chlorinated starches, have generally a considerably lower viscosity than the original starch, and water solutions show less tendency to revert to plastic or gel structures. Such oxidized starches may be directly suitable for laundry use. They are not employed directly as adhesives but as raw materials for further conversion.

Soft pasty products are obtained by treating a starch suspension at a temperature a little below that required for gelation with sodium hydroxide and hydrogen peroxide at a pH of about 10.0 to 10.5. Oxidation takes place at a satisfactory rate. The temperature is increased gradually until gelation occurs. Oxidation may be allowed to continue after gelation or may be terminated by destroying the residual hydrogen peroxide with sodium sulfite or other reagent. The products are sometimes used in the alkaline pH range, sometimes brought to essential neutrality after the oxidation is completed.

Relatively mild oxidations of this type produce viscous liquid adhesives

with only slight plastic properties. The starch molecule is perhaps not greatly degraded by the treatment since dried films are tough, flexible and quite resistant to solution in water. It is a curious phenomenon that prolonging the period of oxidation produces a highly plastic rather than a viscous product. Over-oxidized products may set up so firmly that they can only be removed from a container by cutting.

Other oxidizing agents are sometimes used. Barium peroxide is reported to produce similar results but to provide an adhesive even more resistant to re-solution by water than does the hydrogen peroxide oxidation. It has been said that these products are the barium salts of oxy-starch.

Sodium peroxide is not infrequently used sometimes to effect bleaching rather than actual conversion. Sodium perborate is similarly used, principally for bleaching.

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5C. SYNTHETIC RESIN ADHESIVES

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§ 1. INTRODUCTION. CLASSIFICATION

Synthetic resin adhesives can be broadly divided into two classes; thermosetting adhesives and thermoplastic adhesives.

Thermosetting adhesives are those which, by the application of heat or through the addition of catalysts or by both means, are converted into a substantially infusible and insoluble state. During this conversion, high molecular weight cross-linked compounds are formed. The process is irreversible and the infusible insoluble solid cannot be reconverted to its initial fusible state. Thermosetting resins may be formed by polycondensation reactions, by the polymerisation of molecules containing two or more groups each capable of addition polymerisation, by the polymerisation of polyfunctional molecules or by combinations of these mechanisms.

Thermoplastic adhesives are permanently fusible and soluble. Bifunctional molecules will form linear polymers of this kind, generally by addition polymerisation when the monomer joins to itself to form, initially, a dimer. The dimer then joins with a further molecule of the monomer to form a trimer and addition continues until many molecules are joined together and a polymer is formed. When heated, thermoplastic resins will soften, but harden again on cooling. This process is completely reversible, provided that at any time the polymer is not heated above its decomposition point. Thermoplastic resin adhesives are frequently supplied as solutions of the polymer in an organic solvent. These solutions are easily handled and the solvent serves as a vehicle for uniformly distributing the polymer.

§ 2. ECONOMIC SIGNIFICANCE OF SYNTHETIC RESIN ADHESIVES

Table 16 shows the production and sales in U.S.A. during 1947 of all types of plastic materials and the percentage occupied by adhesives. This table is taken from *Modern Plastics*, January 1949, p. 78—the source of information being the U.S. Tariff Commission.

TABLE 16

PRODUCTION AND SALES OF SYNTHETIC RESINS GROUPED ACCORDING TO USE, 1947
(Quantities and values are based on net resin content only)
Source: U.S. Tariff Commission

	Production		Sales				
	Quantity		Quantity		Value		Unit value \$ per lb.
	1000 lb.	% of total	1000 lb.	% of total	\$ 1000	% of total	
Plastics materials, benzenoid and non-benzenoid							
For protective coatings	453,006	36.2	378,709	33.5	124,423	28.8	0.33
For moulding and casting	312,737	25.0	295,335	26.0	105,633	24.5	0.36
For laminating	45,865	3.7	44,766	3.9	14,327	3.3	0.32
For adhesives	98,346	7.9	93,589	8.2	24,848	5.8	0.27
For treatment of textiles, paper and leather	54,251	4.3	45,660	4.0	17,908	4.2	0.39
For Ion Exchange	7,874	0.6	6,730	0.6	1,705	0.4	0.25
For miscellaneous uses	279,620	22.3	269,950	23.8	142,470	33.0	0.53
Total	1,251,699	100.0	1,134,739	100.0	431,314	100.0	0.38

Exactly comparable figures for Great Britain are not available but Table 17 gives production in tons of various synthetic resins during 1947. The figures are supplied by H. M. Board of Trade and are taken from the *Annual Abstract of Statistics, 1937-1947*, Table 157.

If it is assumed that in Great Britain the production of adhesives is approximately the same percentage of total production as in U.S.A., then it is clear that the development of synthetic resin adhesives in both countries has proceeded at a rapid pace since their introduction in the early and middle 1930s.

The extent to which synthetic resin adhesives have replaced other types of adhesive varies a great deal from country to country. In countries which are predominantly agricultural, supplies of, for example, casein and blood

TABLE 17

PRODUCTION OF SYNTHETIC RESINS IN GREAT BRITAIN DURING 1947

Type	Tons
Phenolic	10,970
Cresylic	11,727
Urea	15,487
Other synthetic resins	2,843
Total synthetic resins	41,027

albumen are readily available and cheap. Facilities for manufacturing synthetic resins are in such cases generally very limited and consequently the degree of replacement of animal and vegetable glues by synthetics is small. In highly industrialised countries where the conditions are reversed, the degree of replacement is relatively large and gradually approaching completion.

Overall however, there is a growing appreciation of the technological superiority and the versatility of synthetic resin adhesives. The resistance of these adhesives to water and their freedom from attack by bacteria and moulds, has enabled for example some types of resin bonded plywood to be used on an increasingly extensive scale both for outside contructional work and under tropical conditions. The realisation, too, of the value of wood as a raw material and of the necessity to bond wood with an adhesive as durable as the wood itself, has also resulted in an increased use of synthetic glues.

The growth of polymer chemistry, the increased understanding of polymerisation reactions and the realisation of the need to relate chemical structure of the adhesive to the nature of the surfaces being bonded, have all contributed to a widening of the field of application of synthetic adhesives. Consequently they are now being used on an increasing scale for bonding materials such as metal, glass and ceramics and give results which compare favourably with conventional and long established processes.

§ 3. THERMOSETTING RESIN ADHESIVES

Industrially, thermosetting adhesives are much more important than the thermoplastic types, since they can be used in highly-stressed structures. The methods of preparation of some of the members of this class are described below. The methods of setting the adhesives and the mechanism by which these processes occur are described in a later section.

(a) *The preparation of Thermosetting Resin Adhesives*

(i) *Phenolic Resin Adhesives*

This group includes all the tar acid-formaldehyde and resorcinol-formaldehyde resins, but details of the preparation of phenol-formaldehyde and resorcinol-formaldehyde resins only, are given.

Phenol-formaldehyde adhesives are, in general, prepared by reacting phenol with a molar excess of formaldehyde (most are prepared with a phenol : formaldehyde ratio of 1 : 1.1 — 2) in the presence of small amounts of alkaline catalysts.

Both hot setting and cold setting phenol-formaldehyde adhesives are prepared in this way—a typical formulation being as follows¹:

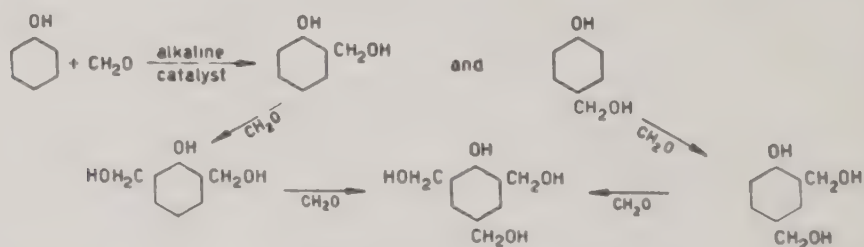
100 kg Phenol
150 kg 30% Formalin
2.5 kg Caustic Soda

are refluxed together for 15 minutes, followed by vacuum evaporation, until a sample of the resin dissolved in an equal weight of acetone has a fixed viscosity.

12.5 kg paraformaldehyde and 25 kg acetone are then added and refluxing continued until a solution of 2 parts by weight of resin dissolved in 1 part by weight of acetone has a viscosity 34–37 times greater than the viscosity of acetone at 20° C.

In the example given the end point of the reaction is determined by viscosity measurement which is essential in a resin from which most of the water has been removed. In other cases the reaction is followed (in the unevaporated resin) by solvent toleration measurements. A fixed volume of the unevaporated resin at, say 20° C, is titrated with solvent, (a mixture of water and methylated spirits is commonly used) until cloudy. The percentage by volume of solvent “tolerated” by the resin can thus be found and this result gives an indication of the extent to which the condensation-polymerisation reaction has continued.

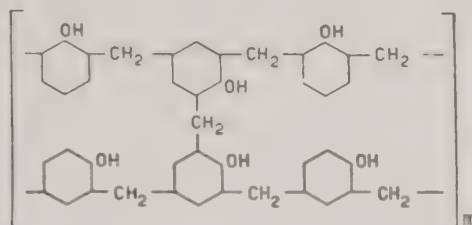
The ability of phenol to take part in such condensation-polymerisation reactions is due essentially to the reactivity of the positions in the benzene nucleus, ortho and para to the hydroxyl group. In the presence of alkaline catalyst, phenol will combine with formaldehyde to form firstly *ortho*- and *para*-hydroxy benzyl alcohols, then 2:4 and 2:6 dimethylol phenols². The formation of 2:4:6 trimethylol phenol has also been suggested³.



The presence of the phenolic hydroxyl is necessary to facilitate these reactions; if this group is acylated or methylated, the reaction with formaldehyde takes place only with great difficulty. POWERS⁴ suggests that a low stage phenol-formaldehyde resin can be represented by a linear molecule

possessing fewer than six phenolic nuclei, methylol groups being present in the reactive positions in the nuclei provided excess formaldehyde is used in the manufacturing process.

The final insoluble and infusible product is represented as a cross-linked macromolecule ⁵.



Degradation experiments carried out by various observers support this contention.

Although the reaction of various phenols with formaldehyde has been investigated extensively, the effects of substituents, (*e.g.* alkyl substituents in the phenol nucleus) on the adhesive properties of the final product has received comparatively little attention.

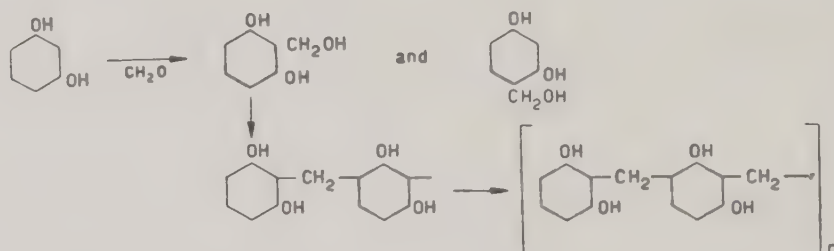
(ii) *Resorcinol-Formaldehyde Adhesives*

Resorcinol-formaldehyde adhesives were introduced commercially in 1943, after very early investigators ^{6, 7, 8} had reported rapid transformation to insoluble products. Resorcinol, having two ortho-para directing hydroxyl groups is consequently doubly activated in the positions ortho and para to those groups and reacts rapidly and easily with formaldehyde. When preparing resorcinol-formaldehyde adhesives, it is therefore customary to react resorcinol initially with considerably less than an equimolecular quantity of formaldehyde, to prevent gel formation.

Numerous patents ^{9, 10, 11, 12, 13} have been taken out on the preparation of resorcinol-formaldehyde resins. In most cases, resorcinol, in a solvent diluent (water serves admirably) is heated to 95–100° C in the presence of a small amount of alkali or acid and then formaldehyde in less than equimolecular amount, added gradually with stirring. When the addition of formaldehyde is complete, the mixture is refluxed for a short time to complete the reaction, evaporated under vacuum and the pH of the adhesive finally adjusted to approximately 7. When the resorcinol-formaldehyde adhesive is used, extra formaldehyde added as paraformaldehyde, provides the methylene groups necessary to complete resinification.

Owing to the speed at which the reaction between resorcinol and

formaldehyde takes place, it is difficult to isolate intermediate products and consequently comparatively little information is available on the structure of these resins. By viscosity measurements and determinations of bromine numbers of reaction mixtures of resorcinol and formaldehyde, DUBRISAY¹⁴ has obtained results which are consistent with the formation of methylol compounds similar to those which are obtained from phenol itself. Such alcohols would presumably condense firstly to form substituted dihydroxy-diphenyl methanes and then further to form a cross-linked network, thus:—



(iii) Urea-Formaldehyde Adhesives

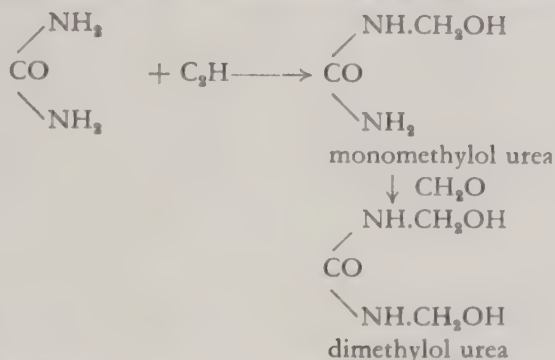
In present day manufacture of urea-formaldehyde adhesives, it is customary to dissolve urea in neutralised formaldehyde, in the molecular ratio of 1 : 1–2, make slightly alkaline, say pH 8–9, and heat for a short period under reflux. The pH of the solution is then lowered to approximately 5 and refluxing continued until dilution, at say 21° C, of a fixed volume of the resin solution with a fixed volume of water produces turbidity. The reaction is first carried out under alkaline conditions to prevent the formation of insoluble compounds such as GOLDSCHMIDT's compound¹⁵ and later carried out under slightly acid conditions, because, as will be described later, the polymerisation-condensation reaction then takes place much more rapidly.

When the required degree of condensation, as determined by the test described above, has taken place, the resin solution is again made neutral and evaporated under vacuum to give a liquid resin of fixed viscosity. Alternatively, the resin solution may be spray dried to give a powder, which is reconstituted by solution in water before use. Various fillers, the use of which cheapens the adhesive without detracting seriously from its adhesive properties, can be mixed into the evaporated liquid or dry-mixed with the powder.

Urea-formaldehyde adhesives are almost invariably used in conjunction with accelerators or "hardeners". The accelerators are usually the ammonium salts of strong acids, such as ammonium chloride, sulphate, nitrate or thiocyanate. These salts in solution react with the free formaldehyde in

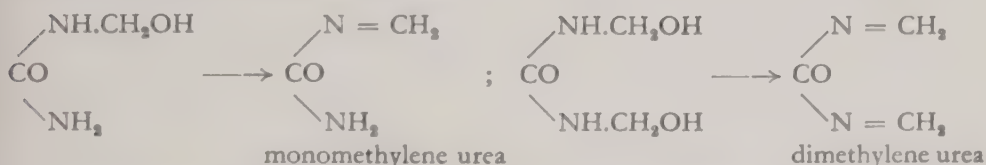
the adhesive and the corresponding strong acid is liberated. The pH of the mixture of adhesive and accelerator is consequently reduced and under such conditions completion of the condensation-polymerisation reaction and the formation of a cross-linked infusible material occurs.

The mechanism of the formation of urea-formaldehyde polymers is still uncertain. Under alkaline conditions, monomethylol urea or dimethylol urea, compounds originally described by GOLDSCHMIDT¹⁶ and EINHORN¹⁷, may be formed depending on the urea/formaldehyde ratio.



It is possible that both these compounds are formed and that there is initially an equilibrium mixture of urea, formaldehyde, monomethylol and dimethylol ureas. Kinetic studies on the reaction of urea and formaldehyde have shown that equilibria of this kind can exist^{18, 19, 20}.

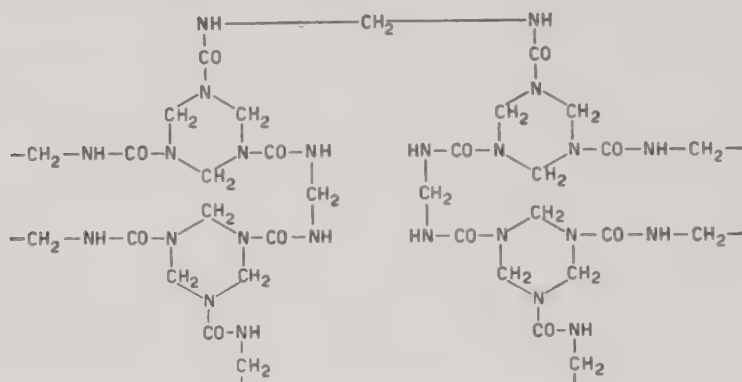
Under acid conditions, the methylol ureas may dehydrate to the corresponding methylene ureas.



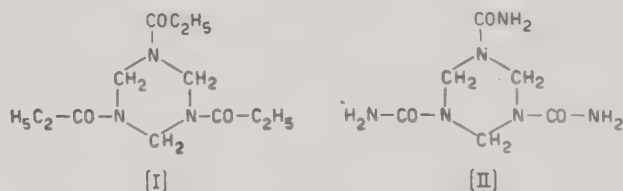
Polymerisation of a difunctional molecule, such as monomethylene urea, would produce a linear polymer, but dimethylene urea, even if present, in small quantities, could act as a cross-linking agent in such chains. Polymerisation of the tetrafunctional molecule, dimethylene urea, would readily give a thermosetting structure. It seems probable that in the evaporated liquid urea-formaldehyde resin, methylol groups are present, as there are indications that amounts of formaldehyde greater than the pure formaldehyde content of the resin can easily be liberated; "additional" formaldehyde could readily be formed by the breakdown of methylol groups.

MARVEL²¹ has suggested an entirely different mechanism of resin formation in which urea reacts as an amino-acid amide, one of the $-\text{NH}_2$ groups

in the urea molecule, thus becoming amine in character and the other amide. The amine group, it is contended, reacts with formaldehyde to yield a methylene-imine derivative, $\text{CH}_2 = \text{NCONH}_2$ which then trimerizes to a cyclic trimethylene triamine compound. The amide $-\text{NH}_2$ reacts with formaldehyde to form methylene bis-amide links between the rings. The final product is postulated as a highly cross-linked structure of the type shown.



MARVEL found that some amino-acid amides will react with formaldehyde in the manner he suggests for urea, and attempts have been made to synthesize the intermediate trimer postulated above. By reacting urethan with formaldehyde the trimer (I) has been prepared—the trimeric nature of this compound being first suggested by GIVA and RACCIN²², and confirmed by MARVEL *et al.*²¹. All attempts to convert the urethan to the urea derivative (II) were however unsuccessful.



(iv) Melamine-Formaldehyde Adhesives

Owing particularly to their greater resistance to water and their better heat stability, melamine adhesives have received considerable attention in recent years.

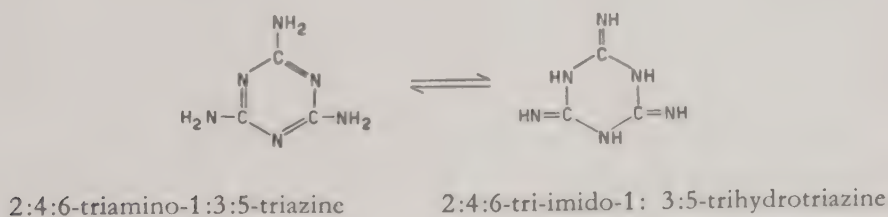
Melamine (2:4:6-triamino-1:3:5-triazine) was first prepared by LIEBIG²³ who was able to isolate it, in small quantities, from among the decomposition products obtained by heating ammonium thiocyanate.

Numerous investigators have since examined methods of preparing melamine, but industrially it is now prepared by heating dicyandiamide under pressure with anhydrous liquid ammonia²⁴. Melamine is a stable crystalline solid, slightly soluble in hot water but only very sparingly soluble in cold water; it melts at 354° C with decomposition and can be sublimed.

A typical method of manufacture of a melamine-formaldehyde resin is as follows²⁵:

Melamine and 40% formalin (in the molecular ratio of approximately 1 : 3) are mixed with stirring and the pH of the mixture adjusted to 8–9 by the addition of dilute caustic soda solution. The temperature of the suspension is gradually raised to 60° C. At this stage an exothermic reaction occurs and the heat evolved is sufficient to raise the temperature of the mixture to about 80° C when solution of the melamine occurs. The solution is maintained at 80° C and the progress of the condensation followed by determining the degree of water toleration. The first stage of the condensation is taken as being essentially complete when permanent turbidity is produced on mixing the resin solution (1 vol.) with water (3 vols.). The mixture is then matured at 80° C for a period equal to that which elapsed between the temperature first reaching 80° C and the occurrence of turbidity on dilution. When the reaction is finally complete, the liquid polymer-condensate is spray or roller dried as its aqueous solution is unstable.

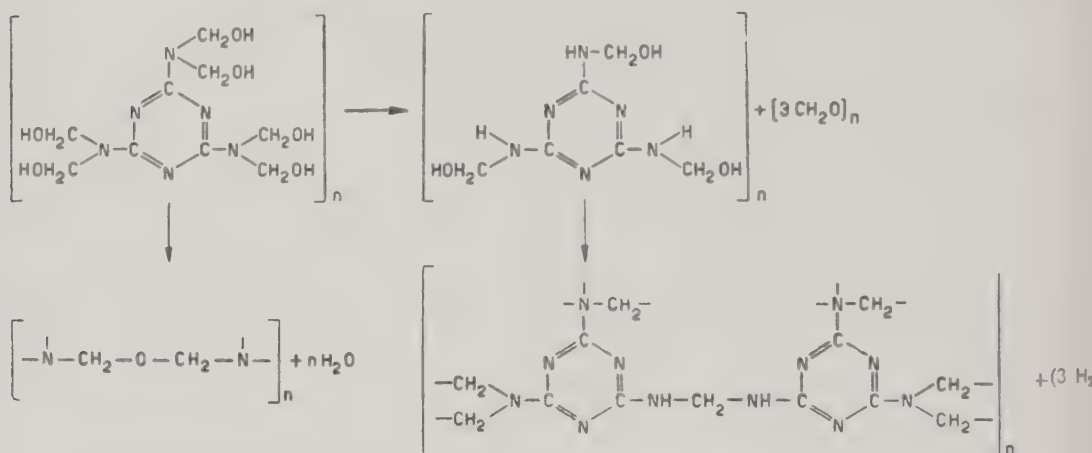
The mechanism of melamine-formaldehyde resin formation has been discussed in detail by KOEHLER^{26, 27} and GAMS *et al.*²⁸. There is some evidence²⁹ that melamine itself can exist as an amide, this form being in equilibrium with the amine form thus:



When discussing the mechanism of resin formation however, it is sufficient to consider the amine form.

Melamine will condense with formaldehyde to form methylol compounds and of the six possible compounds the most stable and most easily isolated is hexamethylol melamine³⁰. A trimethylol compound can also be prepared³¹.

The hexamethylol compound could presumably polymerise through ether ($-\text{CH}_2-\text{O}-\text{CH}_2-$) linkages. If it first lost formaldehyde, and was converted to the trimethylol compound, condensation through methylene links with simultaneous loss of water, could take place. Diagrammatically, this can be represented as shown ³¹:



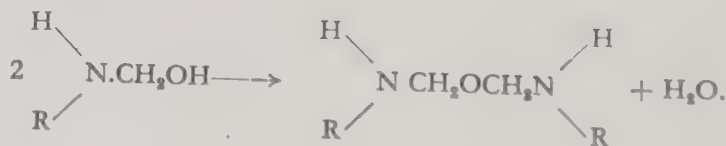
A trimethylol melamine could similarly enter into condensation-polymerisation reactions also with loss of water. It is assumed that in the formation of the melamine resin, the triazine nucleus remains intact, which assumption seems very highly probable in view of the high thermal stability of melamine and its alkyl derivatives.

KOEHLER ²⁶ determined the quantities of formaldehyde and water liberated on long heating of a trimethylol melamine at 180°C . He concluded that practically all the methylol groups reacted with one another and that according to whether water or formaldehyde was split off, either ether or methylene linkages would be produced. From the ratio of water and formaldehyde liberated he calculated that about three ether linkages were present for each methylene linkage.

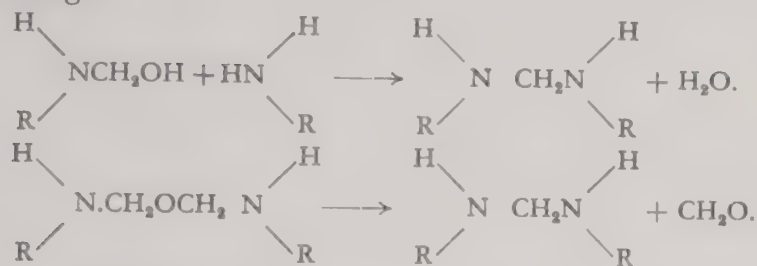
GAMS *et al.* ²⁸ have questioned the method of calculation used by KOEHLER and have pointed out that on the condensation of two methylol groups to form one methylene bridge, both one molecule of formaldehyde and one molecule of water will be split off.

They also point out the possible modes of reaction of a melamine methylol compound which are:

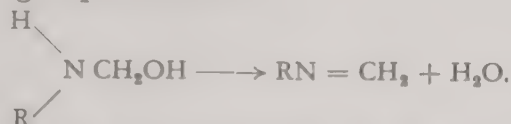
(1) Ether linkage



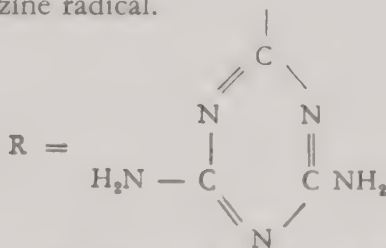
(2) Methylene linkage



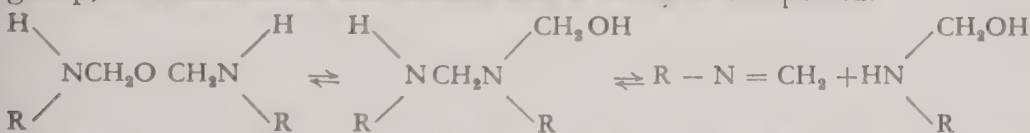
(3) Azomethine group formation



where R represents the diaminotriazine radical.



They further point out that by analytical methods alone, it is not possible to distinguish between an ether link and a methylene plus a methylol group, or a mixture of azomethine and a methylol compound.



These authors finally conclude that it is possible that the ether and methylene bridges act as points where linkage is possible between the molecules and that azomethine groups are also present as potential polymerisation elements.

In a later paper, KOEHLER²⁷ reports the loss of very little formaldehyde on heating the solid resin and again concludes that ether bridges must therefore be formed in preponderance. KOEHLER²⁷ also measured molecular weights of melamine resins and from these measurements calculated that in the unhardened resin four or five triazine rings are present per molecule. The molecular weight rises as hardening proceeds and after five or six hours at 100° C, molecular weight measurements indicate the presence of twelve to fifteen triazine groups.

(v) Miscellaneous Thermosetting Adhesives

Although urea-formaldehyde, melamine-formaldehyde and phenol-formal-

dehyde resins used in aqueous solution form the largest class of industrial synthetic adhesives, there are numerous other thermosetting resins which have been tested for this purpose. It is only possible to give a brief mention of some of them.

a. Furan derivative resins. Furfuraldehyde (furfural) and furfuryl alcohol, the aldehyde and alcohol respectively derived from furan show considerable promise as materials for the production of thermosetting adhesives which can compete successfully with the well established thermosetting materials.

Furfural is obtained commercially by heating bran, obtained from corncobs and oat hulls, with dilute sulphuric acid. The pentoses, which, as pentosanes form a considerable proportion of bran, lose water under these conditions and are converted into furfural.

Furfuryl alcohol is readily obtained by the reduction of furfural. It is also formed, along with furan- α -carboxylic acid when furfural is treated with mild alkalis; the furfural undergoes a CANNIZZARO reaction. In the presence of acid catalysts both furfural and furfuryl alcohol undergo resinification³². Stable liquid polymers can be produced which when activated by the addition of acid catalysts can be cured at room temperature.

β . Polyurethans. A urethan is obtained by the reaction between an *isocyanate* and an alcohol, thus:



Di- or polyisocyanates can be prepared which undergo similar reactions. For example, tolylene di-*isocyanate* is prepared by allowing phosgene dissolved in *ortho*-dichloro-benzene to react with tolylene diamine, the latter being produced by reduction of *ortho*-dinitro-toluene. Polyurethans are then formed by allowing the *isocyanate* to react with polyhydroxy compounds such as 1 : 4-butanediol, hexanetriol, or a polyester containing free hydroxyl groups. The polyester can be prepared by esterification of adipic acid or phthalic acid with *excess* of a polyhydric alcohol, such as glycerol or trimethylol propane. When the polyester is mixed with a di- or polyisocyanate, reaction to form solid compounds of high molecular weight occurs^{33, 34}.

This latter type of reaction was the basis of the German "Polystal" adhesives which were claimed to be not only suitable for bonding wood but also to give promising results in metal to metal joints. These claims have not been wholly substantiated by work carried out in this country, when it was found that a very marked foaming occurred when the polyisocyanate reacted with the polyester and poor bonding resulted.

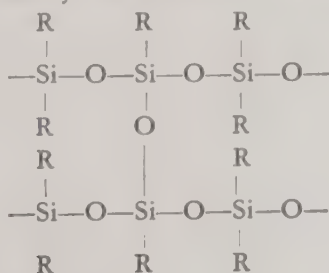
γ. Epoxy-resins. If epoxyethane (ethylene oxide) is allowed to react with acetic acid or acetic anhydride, glycol-diacetate is not the sole product, but diacetates of polyethylene oxides are also formed³⁶. Later attempts to prepare ethylene oxide resins generally gave thermoplastic materials³⁷. It has since been shown that epoxyethane derivatives, which by themselves are thermoplastic, can react further with various compounds and be converted into thermoset materials^{38, 39}.

Suitable epoxyethane derivatives are prepared by reacting, for example, epichlorhydrin with polyfunctional phenols in alkaline solutions, when compounds which have epoxyethane groups at both ends of a carbon chain are produced. Subsequent reaction with organic bases or acid anhydrides, results in cross-linking and the formation of compounds of high molecular weight. The "hardening" process is of interest in that it takes place without the evolution of volatile reaction products such as water or formaldehyde and also without appreciable shrinkage.

δ. Silicone resins. The silicones are heat stable organic silicone oxide polymers, which were introduced commercially during 1944. In chemical constitution they are intermediate between pure organic compounds and the mineral silicates. They possess some of the heat stability of the latter materials and like organic compounds are flexible and soluble in organic solvents.

Initial work on organic silicon compounds was carried out as early as 1904, principally by KIPPING and his collaborators⁴⁰ who were able to prepare organic silicon halides and other organic silicon compounds. By hydrolysis of the organic silicon halides, silicone diols and triols can be obtained which readily polymerise to form long chain and cross linked compounds. To prepare cross linked compounds it is essential that the trifunctional silicone triols should be present. A full description of the various silicone materials now manufactured and their methods of manufacture has been given by BASS⁴¹ and ROCHOW⁴².

ROCHOW and GILLIAM⁴³ were the first to report on the preparation of a solid silicone polymer formed by condensing silicone diols with silicone triols, and which has probably the structure



where R is an alkyl or aryl group.

A variety of silicone resins for the preparation of protective coatings and for electrical insulation are now available. All are characterised by excellent water resistance, an ability to withstand temperatures of approximately 200° C continuously, and good electrical properties.

Although at present their adhesive properties remain to be investigated fully, the silicone resins appear to have potentialities as adhesives for metal-metal, metal-glass and glass-glass combinations particularly where the necessity to withstand high temperatures is essential.

(b) *The Solidification of Thermosetting Resins*

The transformation of a thermosetting resin, from the so called "B stage" (when it will flow under heat and pressure and is still soluble in some solvents) to the "C stage" in which the resin is completely infusible and insoluble, can be achieved in several ways. The most important are:

(1) By the application of heat.

(2) By further condensation caused by the addition of a catalyst.

(3) By the addition of a reagent which either causes the main condensation reaction to continue, (e.g. the addition of paraform to a resorcinolformaldehyde resin), or causes a second reaction to take place (e.g. the addition of "hardeners" to epoxide resins or polyhydroxy compounds to polyisocyanates) the products of which are solids.

When using solutions of phenol-formaldehyde or urea-formaldehyde adhesives, methods (1) and (2) are frequently combined to cause the resin to set quickly. A fixed proportion of catalyst, as stipulated by the manufacturer, is added; the amount being calculated to give a glue/catalyst mixture with a convenient "pot life" at room temperature. By "pot life" is meant the time taken after the addition of catalyst for the resin to reach an "unusable state". This "unusable state" is usually taken to be that at which the resin

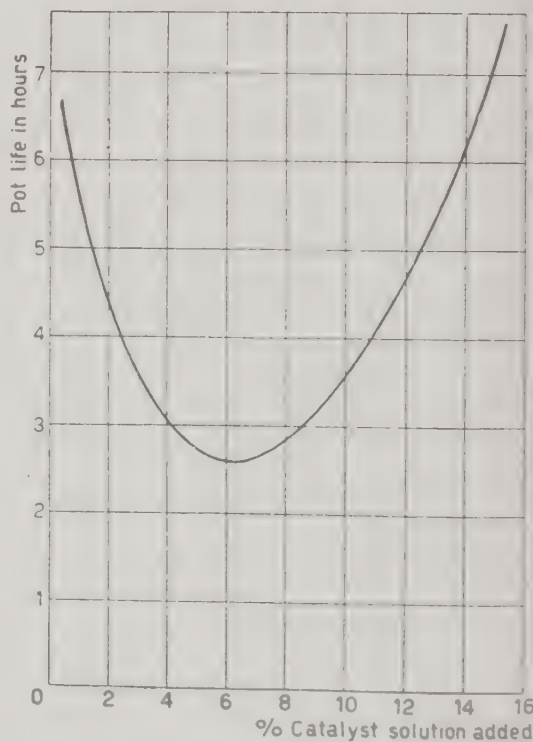


Fig. 77. Variation of pot-life of a urea-formaldehyde resin with increasing addition of catalyst solution.

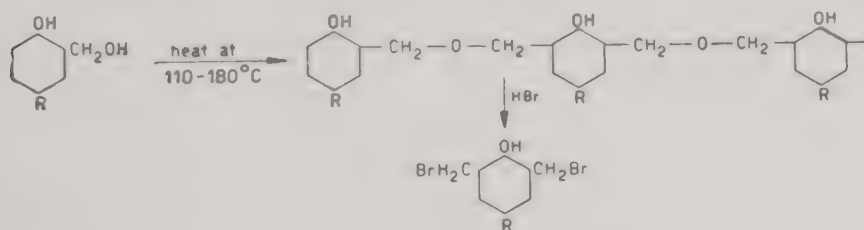
can no longer be spread and corresponds not to a definite viscosity but rather to the inception of a state of high elasticity. Pot-life is different from shelf life, which is the life of a synthetic resin without catalyst.

The pot-life depends on the amount and type of catalyst added to the adhesive and can be varied over a very wide range. If the catalyst consists merely of a single ammonium salt, increasing additions to a urea-formaldehyde resin will produce a decrease in pot-life. If, however, as is frequently the case in practice, the catalyst solution contains both an accelerating agent and a retarding agent, then increasing additions of catalyst solution may give the kind of results shown in Fig. 77, in which the pot-life decreases initially and then increases again with increased catalyst addition. The exact shape of the curve will always depend on the fundamental properties of the resin tested, such as degree of reaction, free formaldehyde content, etc. The same kind of effect has been observed by FREY⁴⁴ using melamine resins.

(i) Phenol-Formaldehyde Resins

A considerable amount of work has been carried out on the mechanism of heat hardening or heat solidification of phenol-formaldehyde resins. By heating pure samples of various phenol mono- and di-methylol compounds and where possible, isolating the products so obtained, it has been found that hardening takes place in stages.

All the workers in this field are agreed that with these resins the first stage of hardening consists of the formation of ether linked polymers by the condensation (with loss of water) of two adjacent methylol groups. For example, on heating the mono- or di-alcohols of ortho or para substituted phenols at temperatures between 110° C and 180° C, ether formation is found to occur.



The presence of ether linkages is shown by treatment with hydrobromic acid in suitable solvents at room or lower temperatures when dibromides corresponding to the initial starting materials are obtained^{45, 46}. If methylene

linkages were present, they would be unaffected by hydrobromic acid under such mild conditions. Owing to the extreme reactivity of phenol itself, most workers use phenols in which some of the reactive positions are already blocked by substituents. This reduces the number of centres of reaction and also the number of compounds which can be formed.

An alternative method of studying the hardening process is to measure the quantities of water and formaldehyde evolved ^{45a, b, c, 46g}. It has been found that the temperatures at which these substances are evolved from a given phenol alcohol are fixed and reproducible and that water is liberated at a lower temperature than formaldehyde.

Considering a simple case, it will be seen that ether linkages can be formed by the elimination of water alone, thus:



Methylene groups are formed by the elimination of both water and formaldehyde as for example:

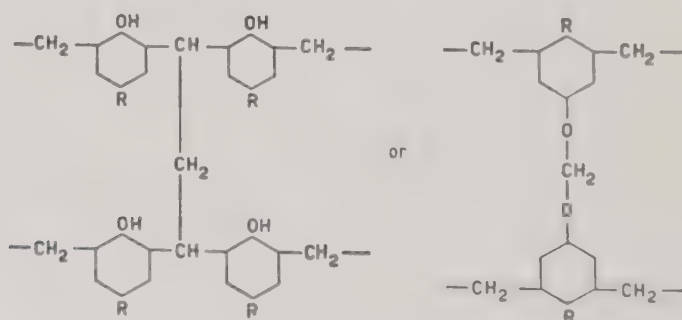


By estimating the weight of water and formaldehyde liberated per gram molecule of the phenyl alcohol, some idea of the ratio of methylene to ether linkages can be obtained. For example, at 150° C methylene bis(4-methyl-2-methylol)phenol, loses 1 molecule of water per molecule of the phenol and only a trace of formaldehyde is evolved at the same time, which is some evidence of preponderant, if not entire, formation of ether linkages.

The mechanism of the conversion or break-down of ether groups to methylene groups is the subject of some disagreement. The formation of a methylene link from an ether link should result in the liberation of 1 molecule of formaldehyde per ether link,

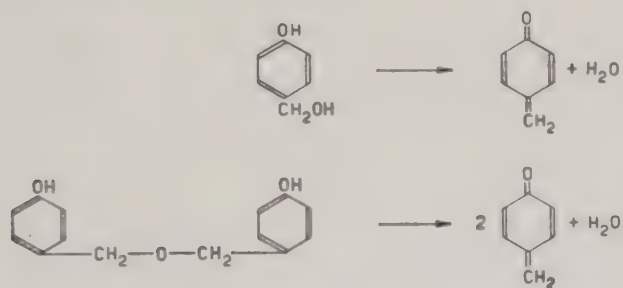


but measurements show that much less is actually obtained. Consequently it has been suggested ^{45c} that part of the formaldehyde reacts at any available reactive position in the phenol rings, or if this is not possible, with methylene bridges or phenolic hydroxyl groups to give structures such as:



Further amounts of water would be liberated by such reactions and have been, in fact, observed. The fact that certain polynuclear phenol dimethylols containing preformed methylene bridges were found on heating to give less formaldehyde and more water per molecule than the simple phenol dialcohols, lends support to this theory. On the other hand, it has been found ⁴⁷ that dihydroxy diphenyl methanes do not react with formaldehyde at 200–240° C—a reaction which might be expected if cross linking by condensation with methylene bridges can occur.

An alternative mechanism of formation of cross linked molecules involving the formation and subsequent polymerisation of quinone methides has been suggested. Quinone methide, the monomer, has never been isolated because it is very unstable and rapidly polymerises. It could be formed from a phenol alcohol or from a dihydroxy dibenzyl ether by loss of water in each case.



This theory is interesting because it indicates a polymerisation reaction

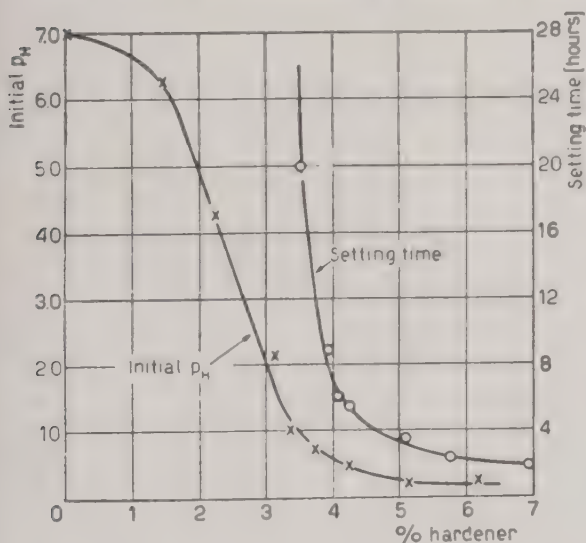


Fig. 78. Variation in setting time and initial pH with hardener concentration for a typical phenolic glue ⁴⁴

rather than a condensation reaction as being at least partly responsible for the formation of a phenol-formaldehyde resin. It is clear however, that the exact mechanism of hardening is still not fully understood and that it may very probably be the result of several simultaneous complex reactions.

The effect of pH on the rate of setting, at room temperature, of a resin prepared from monohydric phenol has been investigated by LITTLE and PEPPER ⁴⁸.

The pH of a mixture of an acid hardener and the resin was determined and the setting time measured by a resistance strain gauge⁴⁹. Curves such as that shown in Fig. 78 were then obtained to show the relation between "initial pH", "setting time" and hardener concentration.

These authors point out that the setting time curve is hyperbolic and setting times become very large at a hardener concentration of about 3.5%, corresponding to a pH of < 1.0 . Above this value of initial pH, setting occurs at room temperature only over a very long period. The same results were obtained when resins based on ortho substituted phenols were used and also when the ratio of formaldehyde to phenol was varied. When meta substituted phenols were used, products which set at a higher pH (a pH as high as 3 is quoted) were obtained, but were much more sensitive to hardener concentrations, *e.g.* the authors state that in this case "increasing the hardener concentration from 5.2 to 5.4% reduced the setting time from one day to one hour". This initial pH above which the resins would not set is described as a "barrier or threshold pH" and is stated to be "a well defined characteristic of all phenolic resins". Fig. 79 shows setting time curves obtained by these authors for a resin at three different temperatures. It will be seen that in all cases amounts of the hardener used of less than about 11% have no effect on the setting time, "indicating that the barrier pH is independent of temperature".

From these experimental results and considering also the work of KROEBNER⁵⁰ and MEGSON⁵¹ and the work of SUGIMOTO⁵², the authors

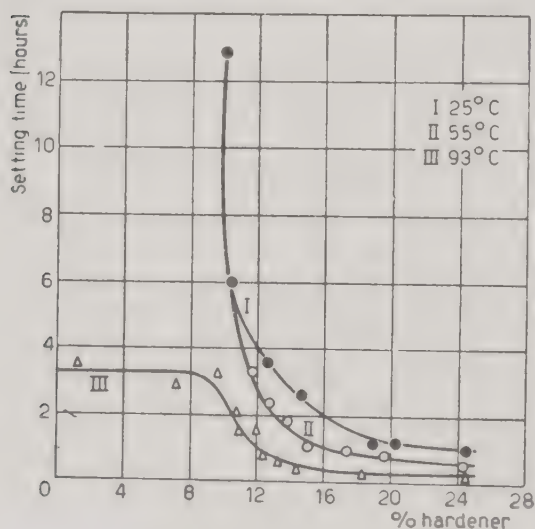


Fig. 79. Variation in setting time with hardener concentration for a phenolic glue at three temperatures⁴⁸

conclude that the acid catalysed setting of phenolic resins depends on the reaction between a phenolic alcohol and a phenol to form a disubstituted methane, the pH required to cause setting being dependent on the state of activation of the reacting groups which itself will be influenced by the other groups present in the molecule.

The fully hardened resins are regarded as rigid three dimensional structures in which there is random cross-linking. HOUWINK⁵³ has suggested that the resin in this state consists of

a continuous macro-molecular skeleton, the pores of which are filled with lower molecular weight condensates and/or unreacted reagents. Other authors⁵⁴ have suggested a spherocolloidal structure in which clumps of macromolecules are entrapped in a continuous viscous liquid disperse phase. More recently BARKHUTT and CARSWELL^{55, 56} studied the structure of the hardened resins by observing the rate of swelling of thin films in acetone, the effects of catalyst concentration, reactant ratios and temperature of cure being examined. As a result of this work, a structure consisting of spherocolloidal particles cross linked to a limited extent by methylene bridges is proposed for the fully cured resin.

(ii) *Resorcinol-Formaldehyde Resins*

When preparing resorcinol-formaldehyde adhesives, it is customary, as already stated, to react one grammolecule of resorcinol with less than one molecule of formaldehyde and to produce final hardening by the addition of a further quantity of formaldehyde, generally added as paraform. This amount of formaldehyde provides the necessary extra methylene groups to complete the cross linking, the hardening process being frequently carried out at pH 7–7.5. When however the pot life of a resorcinol resin, to which has been added a fixed quantity of formaldehyde, is determined at varying pH, and the pot-life plotted against pH, a curve of

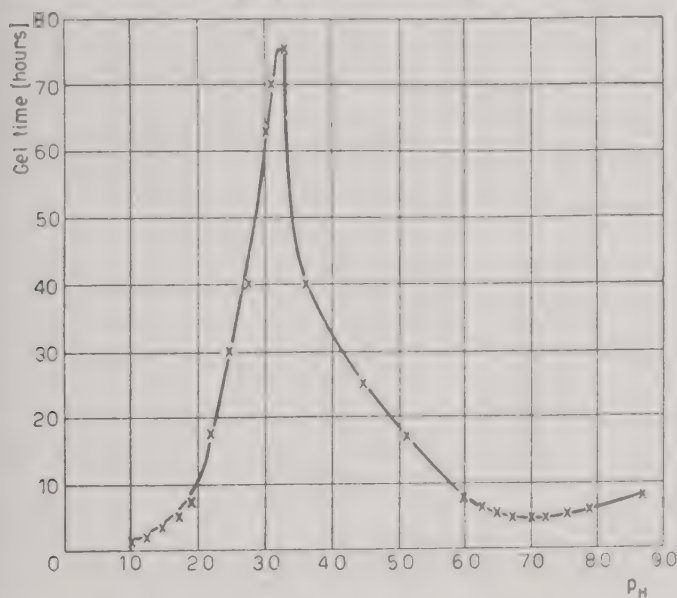


Fig. 80. Variation in gel time of standard resorcinol-formaldehyde syrup with pH⁴⁸.

the type shown in Fig. 80 is obtained⁴⁸.

The curve shows a maximum at about pH 3–4 and a minimum at about pH 7–7.5; the exact pH values corresponding to maximum and minimum pot-lives, depending also on the method of preparation of the adhesive.

According to GRAN-GER⁵⁷ the minimum is due to CANNIZZARO's reaction. LITTLE and PEPPER⁴⁸ explain the maximum by plotting

\log_{10} pot-life or gel time against pH and obtain the graph shown in Fig. 81.

They point out that the two linear portions of the curve indicate two reaction mechanisms, one catalysed by hydrogen ions and the other by hydroxyl ions. The former controls the setting at low pH values, the latter at pH values above 4. In addition, these authors obtained the same type of curve when the resorcinol-formaldehyde ratio of their resins was varied and when the gel times were determined at various temperatures showing that the same reaction mechanisms are operative in all cases.

They suggest that the basic reaction between formaldehyde and a 1:3-dihydric phenols such as resorcinol, to form firstly a phenolic alcohol and then a disubstituted methane may be catalysed by either hydrogen or hydroxyl ions. They further point out that some support for this view is to be found in the fact that the setting characteristics of a range of resorcinol resins prepared at initial pH's ranging from 1-7 were almost identical. Consequently it seems probable that the intermediate compounds—formed either as a result of H^+ or OH^- catalysis—have similar chemical constitution. Experiments carried out by the author tend to show that the initial reaction between resorcinol and formaldehyde is much more sensitive to OH^- than H^+ ions, particularly when the resorcinol: formaldehyde ratio is low.

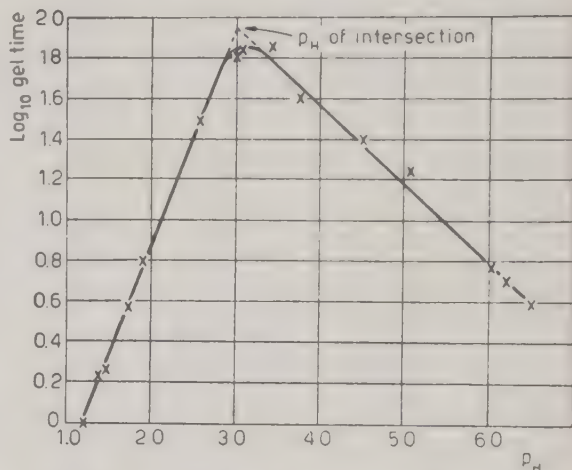


Fig. 81. Standard Resorcinol Formaldehyde Syrup; \log_{10} gel time plotted against pH ⁴⁸

(iii) Urea-Formaldehyde Resins

Some of the chemical reactions involved in the cross linking of urea-formaldehyde resins have already been described. Much less information is available on the precise nature of the compounds formed during solidification of these resins as it is much more difficult to isolate stable intermediate products.

Again it has been found ⁵⁸ that if the pH of a mixture of urea-formaldehyde resin syrup and catalyst is not less than 3.1, then the setting time is greatly protracted. Graphs relating the initial pH and the setting time to hardener concentration are the same type as in Fig. 78 but in this case the "barrier" or "threshold" pH is 3.1.

By plotting \log_{10} (setting time) against initial pH a linear relationship is obtained; the linear relationship holds whatever acid is used as hardener. Hydrogen ion concentration therefore controls the rate of setting and consequently less "strong" acid than "weak" acid is required to cause the resin to set in a specific time. In practice, as has already been stated, it is customary to use solutions of the ammonium salt of inorganic or organic acids as catalysts or hardeners. Typical salts are, ammonium chloride, sulphate, thiocyanate, oxalate and nitrate. Formic, the three chloracetic acids and most inorganic acids can also be used successfully.

As will be discussed later, a large percentage of the urea-formaldehyde adhesives now manufactured is used in the preparation of hot-pressed resin-bonded plywood. For this purpose, it is essential that the $\frac{\text{pot-life}}{\text{pressing time at } 95^{\circ}\text{C}}$ ratio should be large. To achieve this, hardener solutions are frequently compounded so that in addition to, say, ammonium chloride, they contain ammonia, urea and or hexamine. Ammonia and urea are capable of reacting with free formaldehyde in the resin and formaldehyde loosely bound in methylol groups, to form hexamine and a further small quantity of resin respectively. Consequently these substances "compete" with any ammonium salts present for the total available formaldehyde. Decomposition of and liberation of hydrogen ions from the ammonium salt consequently occur to a less extent, the pH of the glue/hardener mix falls more slowly and the pot-life of the glue is extended. It is essential however, that the hardeners formulated to give long pot-life at room temperature should not give glue/hardener mixes which require relatively long pressing times at 95°C —as from a production point of view too long a pressing time is clearly undesirable.

(iv) *Melamine-Formaldehyde Resins*

The setting of melamine-formaldehyde syrups has also been investigated by LITTLE⁵⁸ who found that they could be set readily by the addition of solutions of acids, such as for example, formic, chloracetic, trichloracetic and phosphoric acids. The rate of setting was found to be controlled by hydrogen ion concentration—the \log_{10} (setting time) being related linearly to the pH of the glue/hardener mixture. The "barrier pH" was in this case found to vary between 5.8 and 6.8 depending on the acid used. The melamine resins set therefore under less acid conditions and appear to be somewhat less sensitive to hydrogen ion concentration than the urea-formaldehyde types.

The chemical reactions involved in the setting of various other thermo-

setting resins remain to be fully investigated. Very little information is available for example on the reactions which it is suggested the epoxide resins undergo on addition of the so called "hardeners"—reactions which are of particular interest in that their completion does not result in the formation of volatile products.

(c) Performance and Applications of Thermosetting Resins

Before describing in some detail the performance characteristics of the main synthetic resin adhesives, it is of interest to consider some of the properties required in adhesives particularly when they are used for bonding different types of adherends.

There are two main types of adherend, (a) porous or absorbent, and (b) non-porous or non-absorbent, which give rise to three combinations, (*viz.*: porous to porous, porous to non-porous and non-porous to non-porous) of materials to be bonded together. Frequently, most difficulty is encountered in obtaining satisfactory adhesion between two non-porous adherends.

It can be readily and simply demonstrated that to obtain good adhesion, the adhesive must wet the adherend⁵⁹. It is also approximately true that wetting will occur when the interfacial forces between the adhesive and the adherend are greater than or equal to the cohesive forces of the adhesive. Wetting is therefore a visible sign of the existence of specific adhesion caused by intermolecular attractive forces, which are secondary (VAN DER WAALS') in nature and the magnitude of which, it has been calculated, is sufficient to account for the observed strength of glued joints.

From a more detailed discussion of such forces, DE BRUYNE⁵⁹ has developed the thesis that the behaviour of specific adhesion shows similarities to the rules governing the mutual solubility of liquids as expounded by HILDEBRAND⁶⁰. Just as non polar liquids of low internal pressure tend to be immiscible with polar liquids of high internal pressure so do polar adhesives show incompatibility with non polar solids. In practice, it is usually advantageous to make non polar surfaces hydrophylic by special treatment in order to secure good adhesion. Thus if rubber is immersed in strong sulphuric acid for a short period, it can be glued with a polar adhesive such as a resorcinol-formaldehyde resin.

THINIUS⁶¹ has also discussed the problem of joining different plastics and has shown that the wetting action of the solvent used, plays no significant role in the attainment of good adhesion between adherends, nor does the use of a neutral solvent alone lead to successful results if the

adherends show differing polarities. The author describes new ways for compensating the differing polarities, so that practically every kind of film material can be made to adhere to a differing kind of substrate.

Wetting of the adherend by the adhesive is not sufficient in itself to produce good adhesion particularly if, as is usual, the adhesive eventually solidifies. If when solidification occurs, differential straining between the adherend and the adhesive takes place, internal stresses exceeding the strength of the bond may be set up and bond-rupture will then occur.

Internal stresses may be set up principally (1) by contractions of the adhesive which occur due to solidification reactions, (2) by differences in the coefficients of expansion of the adhesive and adherend when hot-setting adhesives are used, and (3) by the inability of volatiles—present as solvents or liberated during the setting reactions—to escape, particularly from joints made up from non-porous adherends bonded under heat.

Ideally then, synthetic resin adhesives should, if possible, have good wetting properties for all surfaces, should solidify, preferably in the cold, without change in volume and without the evolution of volatile materials. They should, also, be stable, non-corrosive liquids, which can be caused to set in a conveniently short time, by, for example, the addition of another stable, non-corrosive liquid or soluble solid or by the application of moderate heat. In addition, the solid adhesive should itself have good cohesive properties so that it can withstand strain without disintegration and give a bond stronger than the materials being bonded.

Chemically, it is probably essential for an adhesive to be polymeric, and to be composed of both high and low molecular fractions. DELMONTE⁶² suggests that the specific adhesion may be due to the low molecular weight fractions and cohesive properties to the high molecular weight fractions of a given polymer.

Of the three combinations of adherends mentioned above, the most important ones are, (a) metal to metal, (b) metal to wood, and (c) wood to wood, all of which can be bonded satisfactorily with synthetic resin adhesives of various kinds.

(i) *Metal to Metal Bonding*

For bonding metal to metal the ideal adhesive would be one that could be used at room temperature, without the application of more pressure than is required to bring the surfaces into contact, and which in a reasonably short time would give an assembly, which on testing to destruction, resulted in complete metal failure. No material is at present being manufactured which fulfils all these conditions.

Many thermosetting materials used alone are not very successful and consequently, it has generally been found necessary to prepare special adhesives for metal to metal bonding. Some of these consist of a mixture of synthetic rubber and synthetic resin, *e.g.* Cycleweld developed by the Chrysler Corporation, U.S.A., Metalbond, developed by the Vultee Aircraft Corporation, U.S.A., and Pliobond, developed by Goodyear Corporation, U.S.A.

These adhesives can be applied by spraying the metal surfaces (suitably degreased and pickled) until an adhesive layer of recommended thickness has been built up. This layer is allowed to air dry for varying times and then the coated surfaces bonded together under heat and pressure. Pressures varying from 100–1000 p.s.i. and temperatures from 90–160° C are frequently necessary.

In England, a process known as the “Redux” process has been developed by Aero Research Limited. The metal surfaces to be bonded, after degreasing and pickling, are first coated with a low viscosity phenolic resin and then dipped into, or sprinkled with, a thermoplastic polyvinyl acetal powder. Assemblies are pressed for about 15 minutes at 200 p.s.i. and 300° F (150° C) or for longer times at lower temperatures.

An epoxide resin (see page 213), “Araldite”, manufactured by Ciba Limited, Switzerland, can also be used for metal to metal bonding. This resin is supplied in the form of powder or sticks, softens at 40–50° C and is spreadable at 70–100° C. Consequently it is most easily applied to hot metal surfaces, which are then placed in contact; it is not necessary to apply more pressure than is required to maintain surface contact and prevent slipping. The resin is cured by heating for say, 1 hour at 190° C or for longer times at lower temperatures.

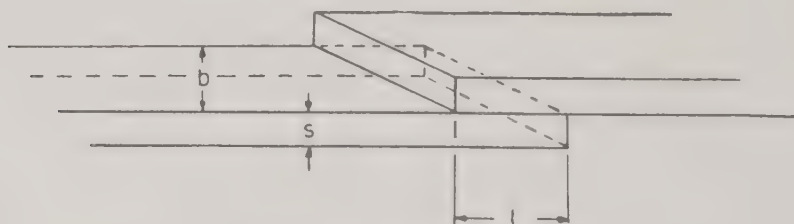


Fig. 82. Simple Overlap Joint

Using Cycleweld, it is stated⁶³ that in bonding sheet aluminium, shear strengths as high as 3000 p.s.i. (calculated on the basis of failing load divided by glue area) have been obtained and the combination of Cycleweld and

a few strategically placed rivets enabled smooth contour assemblies to be made which gave excellent results on test.

Recently, a comparative investigation into the strengths of various types of metal to metal glued joints has been made by HARTMANN ⁶⁴. Table 18 shows some of the results obtained on testing simple lap joints such as that shown in Fig. 82; full details of testing by this method are given in Chapter 9.

TABLE 18

SHEAR STRENGTH OF METAL-METAL JOINTS BONDED WITH VARIOUS ADHESIVES

Metal	Glue	Glue Area in mm ² (b × l)	S in mm	Mean Shear Stress kg/mm ²
Dural	Redux	186	0.5	2.18
"	"	202	0.5	1.93
"	"	135	0.5	2.74
"	"	388	1.0	1.97
"	Araldite	340	1.2	2.22
"	"	148	1.2	3.56
"	"	511	2.2	2.46
"	Pliobond	290	1.2	1.91
"	"	432	2.2	1.13

It will be seen that all these adhesives give metal to metal bonds of considerable strength. It must be emphasised however that to obtain consistently high bond strength, the metal must be pre-treated carefully. When bonding aluminium alloys best results are obtained when the metal is first degreased and then pickled in sulphuric acid/chromic acid mixtures. If instead of being pickled, the metal is degreased and sanded, then although satisfactory results are obtained there is certainly a reduction in the strength of the joint.

It is from developments of this kind that the bonding of metal, in particular aluminium alloys, by synthetic adhesives has now reached a stage where it is, under certain circumstances, able to compete both economically and in performance with the more conventional processes of riveting and welding.

It would frequently be advantageous if the metal bonding could be carried out at room temperature using cold-setting adhesives. One of the "Araldite" resins which sets cold on the addition of a hardener can be used for this purpose. Joints with $\frac{1}{2}$ " overlap, prepared from Alclad test pieces ($1'' \times 4\frac{1}{2}'' \times 0.036''$) and this adhesive will give shear strengths of on the average 6–700 lb. if the metal is degreased and pickled before assembly. If the metal is merely degreased and sanded, a reduction in the strength of the joint occurs. If after bonding, the metal is heated to temperatures greater than 60° C, then the bond strength is reduced.

Resorcinol-formaldehyde resins have also been employed as cold setting metal to metal adhesives but appear to be particularly sensitive to the nature of the metal surface to which they are applied. For example, it has been found in the author's laboratory that using Alclad test pieces of the dimensions stated above and with $\frac{1}{2}$ " overlap, failing loads of, on the average, 1000 lb. can be obtained provided the metal is degreased and pickled very carefully before treatment with the glue and assembly. Under these conditions the adhesion between the glue and the metal is good and failures in cohesion occur. If, however, the metal is degreased and sanded or degreased and etched in mildly alkaline solutions then extremely poor results are obtained and failures are almost entirely due to poor adhesion between the metal and the glue.

(ii) *Metal to Wood Bonding*

Some of the adhesives designed for metal to metal bonding can also be used for bonding wood to metal, provided the pressing or curing temperatures are not detrimental to the wood.

The "Redux" process is well adapted to this purpose. When joints such as those shown in Fig. 82 are prepared using, say, a standard beech test piece ($1'' \times 4\frac{1}{2}'' \times \frac{1}{8}''$) and an Alclad test piece ($1'' \times 4\frac{1}{2}'' \times 0.036''$) with a 1" overlap and then tested in shear to destruction, wood failure invariably occurs.

When the same type of joint is prepared using cold-setting "Araldite", failing loads in shear of 500–700 lb. are generally obtained when the joints are tested to destruction at room temperature. Again, however, the joint strength decreases markedly if the temperature of the assembly is increased.

Wood can also be bonded to metal using a cold-setting resorcinol-formaldehyde resin but to obtain satisfactory and consistent results careful pre-treatment of the metal surface is again essential. When these conditions are satisfied, failure of the wood adherend frequently occurs when the assembly is tested in shear.

(iii) *Wood to Wood Bonding*

By far the largest quantity of synthetic adhesives is used for wood to wood bonding as this includes the manufacture of plywood, an industry which has been revolutionised by the introduction of synthetic resin adhesives.

It is convenient in this instance to distinguish between hot-setting adhesives, which are used for hot-press gluing, and cold-setting adhesives, which are used for assembly gluing at room temperature, even though the same resin adhesive may be employed for both purposes.

a. *Hot-Setting Adhesives.* Synthetic resin adhesives which are caused to set by the application of heat and pressure with or without the addition of a catalyst are now used extensively in the plywood industry.

Most countries stipulate certain performance standards from plywood prepared in this way and in Great Britain these are contained in British

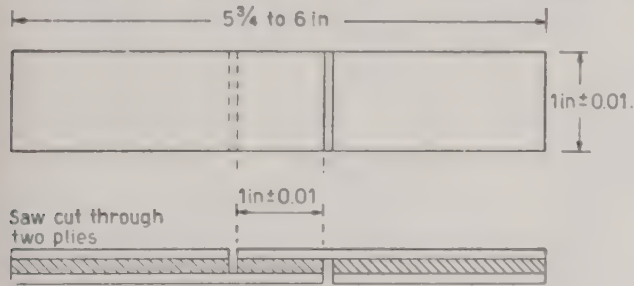


Fig. 83. Plywood Test Piece

Standard 1203. A detailed discussion of the methods of test stipulated by this Specification are given in Chapter 9. It will be sufficient here to describe briefly the type of test piece used. This is shown in Fig. 83*.

These test pieces are prepared by first assembling a 3-ply panel from 1/16" beech veneer using the adhesive under test. This is later cut into strips of the size indicated; saw cuts are then made through two of the plies, the cuts being 1" apart and on opposite sides of the strip.

When pulled to destruction in a standard testing machine both dry and after conditioning in water for varying times and at various temperatures, the test pieces must withstand specified loads. Table 19 gives details of the minimum loads which they must withstand if the adhesive used is to pass the various tests described in British Standard 1203—the mean of six individual tests being taken in each case.

TABLE 19

B.S. 1203 SPECIFIED MINIMUM MEAN FAILING LOADS

Tested Dry	Tested after immersion in water for			
	24 hours at 15–20° C	3 hours at 70° C	3 hours at 100° C	6 hours at 100° C
lb. 250	lb. 250	lb. 200	lb. 100	lb. 200

Some of the first synthetic adhesives suggested for use in plywood manufacture were the phenol-formaldehyde types ⁶⁵, ⁶⁶ and plywood bonded with these will on testing give mean results which are greater than or

* The extracts from British Standards 1203 and 1204 given in Figs. 83, 84 and 85 have been reproduced by permission of the British Standards Institution, which retains all rights of publication and copyright. The Institution does not accept responsibility for the accuracy of the reproduction. Official copies of British Standards may be obtained from the British Standards Institution, 24/28 Victoria Street, London, S.W. 1.

equal to those specified in Table 19. It is however necessary when using these adhesives to press the plywood at temperatures of the order of 140°C and when these resins were first introduced, few plywood manufacturers were equipped with suitable multi-platen hot presses which are essential for this work.

The most popular form of phenol-formaldehyde hot-setting adhesive for plywood manufacture is a thin porous paper sheet coated with the resin and dried ⁶⁷. This dry paper film is interleaved with wood veneers and pressed at about 200 lb. per sq.in. at 140°C for about 4–5 minutes. Such a film is very suitable for many flat hot press operations, ensures uniform distribution of the adhesive at all the glue lines and gives plywood of exceptional water resistance. The high press temperature is necessary to ensure quick cure and adequate flow of the phenol-formaldehyde resin. The coated film technique tends therefore to be limited to some extent to the production of thin plywood. If it is used in making thick plywood, the time required in the hot press to ensure that the innermost plies are at 140°C may be sufficient to be detrimental to the surface plies. This difficulty can however be overcome by using the more recently developed dielectric heating processes.

Liquid phenol-formaldehyde resins are also used for making plywood but at press temperatures of 140°C , become very fluid and tend to penetrate into the wood. When this occurs poor adhesion frequently results. Attempts have been made with some success to reduce penetration by adding to the phenol-formaldehyde resin, starch fillers which gelatinise quickly in the hot press and increase the viscosity of the hot glue/filler mixture.

Phenol-formaldehyde resin bonded plywood is both weather and mould-resistant and consequently was used extensively in World War II in the manufacture of wooden aeroplanes, gliders and boats. As a material for outside constructional work, it is nowadays finding more and more extensive application.

Urea-formaldehyde resins are also used in considerable tonnage as hot-setting plywood glues and have the advantage of low cost and of requiring press temperatures of only about 95°C , which temperature can usually be obtained in presses originally designed for use with hide or vegetable glues. The low press temperature required facilitates the preparation of thick plywood and reduces appreciably the chances of penetration.

Plywood bonded with urea-formaldehyde resin has only relatively poor resistance to water at temperatures greater than 70°C . It will withstand prolonged immersion in water at ordinary temperatures or immersion in water at 70°C but in general will fall apart after immersion in water at

TABLE 20

AVERAGE RESULTS OF SHEAR TESTS ON THREE-PLY $\frac{3}{16}$ INCH BIRCH PLYWOOD SPECIMENS, GLUED WITH A UREA-FORMALDEHYDE RESIN GLUE FORTIFIED WITH RESORCINOL, BEFORE AND AFTER BOILING, IN WATER

Glue number	Relative parts by weight		Number of specimens tested	Dry ^a	Wet ^b	Boiling period ^c			
	Urea resin	Resorcinol				3 hours	6 hours	9 hours	12 hours
1	100	0	120	^d 477-91	^d 573-96	^d 150-1	^d 54-1	^d 42-1	^d 23-0
2	93	7	126	504-92	635-99	344-0	271-1	208-1	204-0
3	87	13	120	523-88	657-100	453-42	428-32	394-11	391-7
4	80	20	120	536-88	671-100	499-77	481-98	445-65	465-65
5	73.5	26.5	120	516-94	601-100	536-91	491-49	492-84	469-69
6	62	38	120	443-99	576-100	549-95	508-85	515-72	495-23

^a Tested dry after conditioning at 80° F and 65 % relative humidity.

^b Tested wet after soaking in water 48 hours.

^c Tested wet after boiling for the period designated.

^d The first figure is the shear strength in pounds per square inch; the second figure is the wood failure in percent.

TABLE 21

AVERAGE RESULTS OF SHEAR TESTS ON THE-PLY $3/16$ INCH BIRCH PLYWOOD SPECIMENS, GLUED WITH A UREA-FORMALDEHYDE RESIN GLUE, FORTIFIED WITH MELAMINE RESIN BEFORE AND AFTER BOILING IN WATER

Glue number	Relative parts by weight		Number of specimens tested	Dry ^a	Wet ^b	Boiling period ^c			
	Urea resin	Melamine resin				3 hours	6 hours	9 hours	12 hours
1	100	0	156	d 433-98	d 480-99	d 113-3	d 8-0	d 0-0	d 0-0
2	95	5	36	462-97	396-100	183-5	133-3	83-0	20-0
3	90	10	36	428-95	484-94	302-5	212-0	196-0	160-0
4	85	15	36	589-98	495-95	382-42	276-17	225-6	215-1
5	80	20	120	454-100	518-100	421-78	339-30	302-21	330-32
6	60	40	120	438-100	454-99	425-96	392-85	370-68	363-75
7	40	60	120	472-95	498-100	431-89	408-78	410-80	409-73
8	20	80	120	455-54	513-91	474-93	447-56	440-60	430-62
9	0	100	120	419-57	495-97	518-95	449-87	445-86	434-92

^a Tested dry after conditioning at 80° F and 65 % relative humidity.

^b Tested wet after soaking in water 48 hours.

^c Tested wet after boiling for the period designated.

^d The first figure is the shear strength in pounds per square inch; the second figure is the wood failure in percent.

100° C for relatively short times. Many attempts have been made therefore to fortify urea-formaldehyde adhesives and so improve their resistance to hot water. This can be achieved to varying extents by the addition of resorcinol⁶⁸, melamine⁶⁹ or melamine-formaldehyde resins.

Tables 20 and 21 taken from a U.S. Forest Products Research Laboratory Bulletin⁷⁰ show the degree of boiling water resistance which can be imparted to urea-formaldehyde resins fortified with resorcinol and melamine resin respectively, when used for making birch plywood which is then tested in shear and in tension.

It is stated that using additions of resorcinol the panels were pressed for 4 minutes at 280° F and a pressure of 250 lb. per sq.in. When using additions of melamine resin, the panels were pressed for 8 minutes at 280° F. In both cases the pressing temperature is higher than that usually employed with urea-formaldehyde adhesives.

Attempts made at Aero Research Limited to reproduce the results given in Table 20 but using a pressing temperature of only 95° C and beech veneers have not been entirely successful except when the pH of the resorcinol/urea formaldehyde resin mixture was lowered considerably. It would appear that the added resorcinol is capable of combining readily with free formaldehyde in the urea-formaldehyde glue and possibly too with formaldehyde present as methylol groups to produce a urea/resorcinol co-polycondensate. This theory is supported by the fact that attempts to use simple mixtures of urea-formaldehyde and resorcinol-formaldehyde resins to impart boiling water resistance are not successful even when relatively large amounts, say up to 20% by weight of resorcinol-formaldehyde resin, are added.

The addition of melamine, melamine salts⁶⁹ or melamine-formaldehyde resin to urea-formaldehyde adhesive also improves its boiling water resistance. The maximum amount of fortifying which can take place is that which produces specimens which give 100% wood failure when tested. The addition of fortifying agent required to do this will clearly depend on the wood used. Consequently it is not possible to quote a definite percentage of fortifying agent as being that required in all cases to produce plywood which will pass the tests specified in B.S. 1203.

There is evidence however⁷¹ that increasing additions of melamine to urea-formaldehyde resin do not produce increasing resistance to boiling water once an optimum amount has been exceeded and when relatively short pressing times (say 10 minutes) are given. It seems probable that when sufficient melamine has been added to combine with free formaldehyde or formaldehyde present as methylol groups in the urea-formaldehyde resin

then maximum fortifying effects result. Further additions of melamine are then equivalent to the addition of a soluble filler and may be detrimental. By increasing the pressing time or by alteration of the pH of the urea-formaldehyde resin/melamine mixture the optimum addition may be altered and fortifying effects greater than those obtained with short pressing times may be obtained.

When urea-formaldehyde resin is fortified by continued and increasing additions of melamine resin, progressive increase in boiling water resistance occurs until, when the proportion of melamine-formaldehyde resin is preponderant, complete resistance to boiling water is obtained. At present melamine-formaldehyde resins are relatively expensive even after "extension" with fillers such as rye flour and consequently they are not widely used in the plywood industry except where their particular properties are required.

When urea-formaldehyde resins were first used for making plywood, it was common practice to "extend" and cheapen them by adding relatively large quantities of fillers such as rye flour. Dilution of the resin in this way was found to produce little reduction in the dry strength of the plywood, although its wet strength deteriorated rapidly with increased flour addition.

The introduction of new materials to an industry almost invariably introduces at the same time new problems and the use of synthetic resins for making plywood is no exception. The possibility of penetration of the resin into the wood has already been mentioned and this phenomenon is always likely to occur especially when bonding veneers of high moisture content. Dilution of the synthetic glue by moisture in the wood may result in the viscosity of the glue being lowered to such an extent that excessive penetration and joint starvation take place. In addition, moisture present in the glue line during setting may cause precipitation of the resin itself so that it hardens as separate particles, and not as a continuous film, causing appreciable reduction in joint strength.

With hot-setting adhesives, the condition known as pre-curing may also arise, when the resin is partially cured before full contact between the surfaces is obtained. Pre-curing can result in complete lack of adhesion but more commonly produces small patches or blisters. To prevent this, rapid loading of the press is essential (although not always easy to achieve in practice) as the heat from the platens soon raises the temperature of the veneer to that at which the quick setting associated with synthetic resin adhesives commences. Blisters may also be formed, particularly when using high press temperatures, by too rapid release of pressure at the end of the curing cycle. This allows sudden conversion of hot water under pressure (and consequently below its boiling point) to steam, when the pressure is

released. If the steam cannot all escape quickly through the pores of the wood, it may, in places, force the veneers apart and cause blistering. It is essential therefore in these circumstances to reduce pressure slowly so that the rate of steam formation is reduced and the steam can then diffuse away harmlessly through the wood.

β. Cold-Setting Adhesives. Cold-setting synthetic resin adhesives are designed for use in assembly gluing where it is difficult and sometimes impossible to apply heat and pressure to the parts being glued. For this purpose urea-formaldehyde, resorcinol-formaldehyde and to a lesser extent phenol-formaldehyde resins are employed—a catalyst or hardener being added to the adhesive before use. Much stronger catalysts are required than for hot-setting adhesives and consequently the pot life of the mixture of cold-setting resin and hardener may become inconveniently short.

This difficulty can be overcome in urea-formaldehyde adhesives by applying the catalyst to one of the surfaces to be joined and the resin to the other so that interaction does not begin until the joint is closed ^{72, 73}. This technique, conveniently described as “separate application” is less adaptable to cold-setting phenol-formaldehyde adhesives which may require catalysts of such a strength that their separate application to wooden surfaces might be harmful.

Thick films of urea-formaldehyde adhesives tend to crack or craze and where there is the possibility that joints may be made without adequate pressure, fillers are added ^{74, 75} or special hardeners ⁷⁶ are used. Fillers are also added to resorcinol-formaldehyde and phenol-formaldehyde resins in similar circumstances.

Specific tests are contained for cold-setting adhesives in B.S. 1204. Two types of joints are tested for shear strength; simple overlap close contact joints to which pressure can be applied, shown in Fig. 84, and „gap joints” shown in Fig. 85;

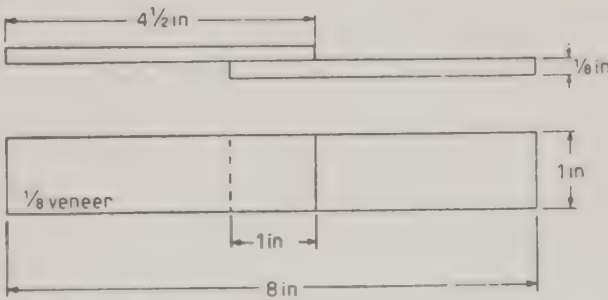


Fig. 84. Close Contact Test Piece

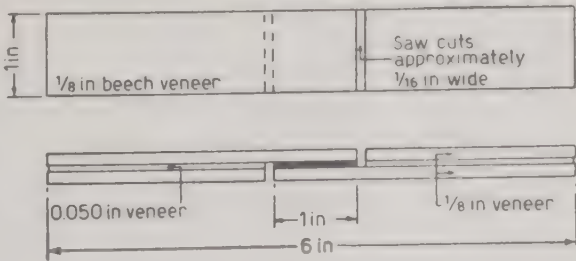


Fig. 85. Gap Test Piece

beech wood being used in both cases (for further details of this test see Chapter 9).

Table 22 gives the specified minimum failing loads for the joints when dry and after immersion in water at various temperatures.

TABLE 22

B.S. 1204 SPECIFIED MINIMUM MEAN FAILING LOADS

Illustration of Test Piece	Tested Dry	Tested after immersion in water for		
		24 hours at 15–20° C	3 hours at 70° C	3 hours at 100° C
Fig. 85	600 lb.	450 lb.	325 lb.	325 lb.
Fig. 86	450 lb.	400 lb.	225 lb.	225 lb.

Test pieces prepared from cold-setting urea-formaldehyde adhesives will certainly give failing loads greater than or equal to those specified in Table 22 when tested dry. Under these conditions failure of the wood rather than failure of the glue almost invariably occurs. Whether used as hot-setting or cold-setting materials, urea-formaldehyde resins will not withstand boiling water for an appreciable time and resorcinol-formaldehyde glues must be used if hot water-resistance is required in the assembly.

Resorcinol-formaldehyde resins combined with a hardener, consisting of paraform and a filler, will give both close contact and gap joints which can be immersed in boiling water for many hours and on testing still withstand loads greater than the minimum failing load specified in Table 22. Again failure of the wood adherends and not the glue, limits the maximum load which can be applied to such assemblies.

Cold-setting synthetic adhesives are now widely used throughout the wood-working industries and in addition to replacing vegetable and hide glues to an appreciable extent, have also by virtue of their unique properties made possible many advances in the technique and art of assembly gluing.

§ 4. THERMOPLASTIC RESIN ADHESIVES

Thermoplastic adhesives are not as important industrially as the thermo-setting types. This is due mainly to (1) their tendency to "cold flow" when subjected to a static load for long periods, and (2) the relatively large decrease in the strength of the bond between adherends which occurs with increase in temperature and which results from softening of the adhesive.

The methods of preparation and the performance of only the more important members of this class will be discussed.

(a) *Preparation of Thermoplastic Resin Adhesives*

(i) *Polyvinyl Resins*

Vinyl acetate is prepared by passing acetylene through glacial acetic acid containing a catalyst such as mercuric sulphate, phosphate or acetate. The temperature is maintained at about the boiling point of vinyl acetate (74° C) so that as fast as this compound is formed, it distils over. Any excess acetylene is re-circulated and allowed to react again. If the reaction temperature rises appreciably above 70° C, then ethylidene diacetate, formed by combination of vinyl acetate and acetic acid, tends to become the main reaction product.

The two reactions can be represented thus:



If it is necessary to store the vinyl acetate, then a small amount of a copper or iron salt or a sulphur compound is frequently added to prevent polymerisation, and must be removed again before polymerisation is attempted.

The highly purified monomer, mixed with a solvent is polymerised by maintaining it at its boiling point for a period of several hours. The solvent and any unpolymerised vinyl acetate can be removed by distillation or steam distillation and the polyvinyl acetate finally extruded and shredded.

When used as an adhesive, polyvinyl acetate is often supplied as an aqueous emulsion or dispersion prepared by polymerising an emulsion of vinyl acetate in the presence of an organic peroxide. Stable dispersions can be prepared by polymerising in the presence of an emulsifying agent and a hydrophilic colloid ⁷⁷.

The degree of polymerisation of polyvinyl acetate depends upon factors such as temperature, the nature and quantity of solvent and the catalyst ⁷⁸. In general, if the polymerisation is carried out at a high temperature, low molecular weight material is obtained. When vinyl acetate is polymerised in solution, lower molecular weight products are formed as the concentration of vinyl acetate in the solution increases. With small quantities of a catalyst such as acetyl peroxide, higher molecular weight products are obtained but as the concentration of catalyst increases so the molecular weight of the polymer tends to decrease.

The molecular weight of the polyvinyl acetate also depends to an appreci-

able extent on the solvent used, when polymerisation is carried out in solution. BLAIKIE and CROZIER⁷⁸ found that highest molecular weight compounds, (as measured by the viscosity of the solution) were obtained using benzene as solvent and the lowest using toluene—a surprising result considering the similarity of these two solvents. Compounds of intermediate molecular weight were obtained when solvents such as acetone, alcohol, acetic acid and ethyl acetate were used.

Owing to wide variations in the degree of polymerisation, polyvinyl acetate sold under trade names frequently carries a suffix which denotes the viscosity in centipoises of a benzene solution of the material containing 86 grams per litre.

An ethylene derivative such as $\text{CH}_2 = \text{CXY}$ (in the case of vinyl acetate $\text{X} = \text{H}$ and $\text{Y} = \text{CH}_3\text{COO}-$) can theoretically yield three types of linear polymer:

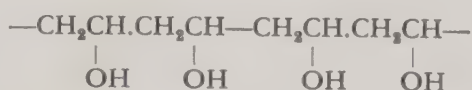
- (1) $-\text{CH}_2\text{CXY}.\text{CH}_2\text{CXY}.\text{CH}_2\text{CXY}-$ (head to tail type)
- (2) $-\text{CH}_2\text{CXY}.\text{YXCCH}_2\text{CH}_2\text{CXY}.\text{YXCCH}_2-$ (head to head type)
- (3) $-\text{CH}_2\text{CXY}.\text{CH}_2\text{CXY}.\text{YXCCH}_2.\text{CH}_2\text{CXY}-$ (random or irregular type)

and most ethenoid polymers appear to be of the “head to tail” variety.

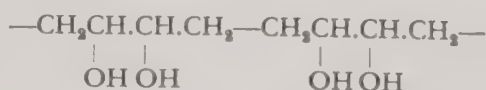
Polyvinyl acetate would, if “head to tail”, have a structure



and polyvinyl alcohol to which it is hydrolysed (a reaction which can be readily carried out) a structure



in which any two consecutive hydroxyl groups would be in the position 1 : 3 to each other (a 1 : 3 diol). A “head to head” structure would give polyvinyl alcohol with a structure

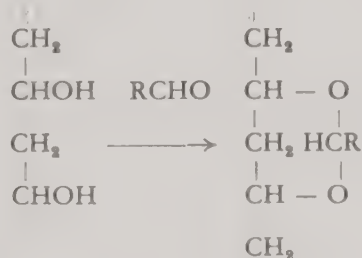


in which any two consecutive hydroxyl groups would be in the 1 : 2 position to each other (a 1 : 2 diol).

Periodic acid produces specific oxidative fission of 1 : 2 diols but was shown⁷⁹ to have no effect on polyvinyl alcohol, indicating a 1 : 3 diol structure.

X-ray examination has confirmed this⁸⁰ but later work on periodic acid oxidation has lead McLAREN and DAVIS⁸¹ to deduce that there are a few "head to head" links on a predominantly "head to tail" structure. It is extremely improbable that hydrolysis of polyvinyl acetate to polyvinyl alcohol could bring about alteration in structure and consequently the "head to tail" structure shown for polyvinyl alcohol can be assigned to polyvinyl acetate.

Polyvinyl alcohol produced by hydrolysis of polyvinyl acetate will react with aldehydes in the presence of an acid catalyst to form polyvinyl acetals. These compounds contain stable six membered rings formed by reaction between the aldehyde and the hydroxyl groups of the polyvinyl alcohol thus:



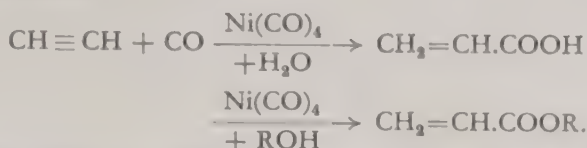
When fabricated into sheet form such materials are tough and rubbery. They have been developed primarily by Shawinigan Chemical Company Ltd.; the materials obtained from polyvinyl alcohol, formaldehyde, acetaldehyde and butyraldehyde being known as Formvars, Alvars and Butvars respectively.

(ii) *Acrylic Resins*

Early work on acrylic acid esters was carried out by ROHM⁸² as early as 1901, but the methacrylate polymers have been available in sheet and powder form only since about 1937.

In the preparation of acrylic compounds, ethylene is reacted with hypochlorous acid to form ethylene chlorhydrin which on treatment with sodium cyanide gives ethylene cyanohydrin. This compound is dehydrated to form acrylonitrile which in turn is hydrolysed to acrylic acid. If the dehydration of ethylene cyanohydrin (generally by sulphuric acid) is carried out in the presence of an alcohol, the acrylic ester⁸³ corresponding to the alcohol present is formed.

mical method of synthesising these compounds. The reactions can be represented as follows:



Acrylic and methacrylic esters can be polymerised by acids, heat, ultra violet light and organic peroxides, the acrylic esters polymerising with greater ease. Special emulsion polymerisation techniques have also been worked out in an effort to produce the polymers in a finely dispersed condition.

When methacrylic esters are polymerised by benzoyl peroxide the polymerisation reaction is preceded by an induction period. The induction period and the time for 95% of the material to polymerise has been found⁸⁶ to decrease with increasing concentration of catalyst and increasing temperature.

When methyl methacrylate is polymerised in solution, the nature of the solvent influences to a considerable extent the degree of polymerisation obtained. STRAIN⁸⁶ found that 50% aqueous methanol used as solvent gave much higher molecular weight material than any other solvent tested and in addition the polymerisation proceeded most rapidly under these conditions. 50% aqueous methanol is a solvent for the monomer, but not for the polymer, a condition which frequently appears to give rise to higher molecular weight polymers.

(iii) Cellulose Esters

In the search for useful cellulose derivatives, the cellulose esters of most commercially available acids have been prepared. As adhesives, cellulose nitrate (nitro-cellulose), cellulose acetate and to a lesser degree cellulose acetate-butyrate (a mixed ester prepared from cellulose and acetic/butyric acid mixtures) have attained industrial importance.

Cellulose nitrate is prepared by the nitration of cellulose, usually in the form of cotton linters, with mixtures of sulphuric acid, nitric acid and water, the exact composition of the nitrating mixture depending on the nitrogen content and properties required in the nitrated product.

The nitration is carried out at a carefully controlled temperature and when it has proceeded to the desired extent, the ester is centrifuged to remove excess acid and then washed with water until acid free. The water is then removed by repeated washing with alcohol, plasticizers, such as

camphor added and when solutions are required, the cellulose nitrate/plasticizer mixture dissolved in a suitable solvent or a mixture of solvents.

For some applications it is essential that the degree of polymerisation of the cellulose ester should vary between only quite narrow limits. This can often be achieved by careful choice of the cellulose used and by controlled thermal degradation of the ester before purification. In this way, for example, solutions of relatively high solids content but comparatively low viscosity such as are required for lacquers can be obtained.

Cellulose acetates, can be prepared by treatment of cellulose from cotton linters or from selected paper pulps, with a mixture of acetic anhydride, acetic acid and sulphuric acid at temperatures of 20–40° C.

The triacetate, which is eventually formed and which is soluble in the reaction mixture is unsuitable for many applications. However by addition of dilute acetic acid to the reaction mixture until 5–10% water is present, hydrolysis to the diacetate occurs. The diacetate can be precipitated by the addition of excess water, filtered, washed, stabilised and dried.

There is some evidence that the sulphuric acid reacts initially with the cellulose to form cellulose sulphates which then react readily with acetic anhydride. As acetylation proceeds, gradual replacement of sulphate groups by acetyl groups occurs, giving compounds of increasing acetyl content until the triacetate (acetyl content 42.5–44.5%) is obtained. The final product must be obtained free from cellulose sulphates as these compounds tend to make cellulose acetate unstable.

Mixed cellulose esters can be prepared using a mixture of the appropriate acid anhydrides. A mixed ester such as cellulose acetate-butyrate has the advantages over pure cellulose acetate of being soluble in a wider range of solvents, miscible with a wider range of plasticizers and of possessing better water resistance.

That there should be many variations on the general methods of preparation of both cellulose nitrate and cellulose acetate is only to be expected and it is impossible to attempt to describe such variations here. Different methods of pre-treatment of the cotton linters both with a view to facilitating acylation and where necessary preserving their fibrous structure and methods of heterogeneous acylation, are among the modifications which have been developed.

(b) The Setting of Thermoplastic Resin Adhesives

Three main methods of setting thermoplastic adhesives can be distinguished, namely:

- (1) Solidification of the molten polymer.
- (2) Solidification of a solution of the polymer by evaporation or diffusion of solvent, generally at atmospheric temperature.
- (3) Solidification of a mixture of a catalysed monomer and polymer or of a partially polymerised monomer.

The first method should be capable of giving excellent bonding even of non-porous adherends as in the process of fusion and subsequent solidification of the thermoplastic material no volatiles are evolved. Consequently stresses caused by the inability of volatiles to escape from between non-porous surfaces should be avoided. In addition it should be possible to obtain a bubble-free, strain-free bond which retains enough flow to compensate for temperature differentials and for differences in coefficients of thermal expansion between adhesive and adherend.

Since thermoplastic adhesives such as polyvinyl acetate, cellulose nitrate, etc., are frequently supplied dissolved in a solvent, solidification takes place most commonly by solvent evaporation.

Correct choice of solvent is important it as is desirable that the solution should have a fairly high solids content, so that an adequate amount of adhesive can be applied in a single coat and a fairly low viscosity so that it can be easily handled and spread. It is also important that the rate of evaporation of solvent should be high so that most of the solvent is lost when open assembly times are relatively short. These two factors tend to be antipathetic since it is probable that if a solvent is a sufficiently good one for a particular polymer to enable a solution of high solids content to be made, then the retention of relatively small amounts will be sufficient to maintain the polymer in partial solution and prevent true solidification.

One of the most important problems associated with the use of thermoplastic adhesives in solution with non-porous adherends is the evaporation of solvent from the film or glue line. The presence of unevaporated solvent or volatiles will reduce appreciably the strength of the joint. The problem is particularly acute where large areas are being bonded in which case the area containing solvent is relatively large compared with the perimeter of the bond which is the only region from which solvent evaporation can take place, once the adherends have been united. It seems probable that in many such cases the bond depends largely on "edge sticking" for its strength. Clearly these difficulties do not arise if one of the adherends is porous and allows slow diffusion of solvent through the area being bonded.

To reduce strains set up in a joint due to the presence of unevaporated solvent it is customary to air-dry adherends before assembly. There is

clearly an optimum time of air-drying for each adhesive. If this is exceeded, the adhesive loses its initial tack or in extreme cases forms a solid layer. Good adhesion can then only be obtained by heat welding techniques. If

air-drying is not allowed to continue for a long enough period, then as already discussed, relatively weak bonds will be obtained.

Fig. 86 shows the results obtained by DELMONTE⁸⁷ who examined the shear strength of steel blocks bonded with polyvinyl acetate solution, after different open assembly times at 25° C.

It will be seen that immediate assembly results in low strength, maximum strength is obtained after partial evaporation of solvent and that when open assembly times are too

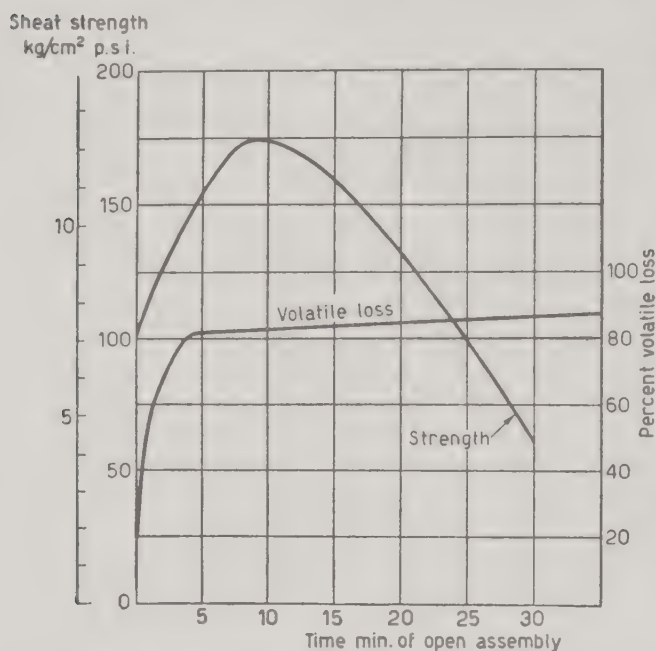


Fig. 86. Polyvinyl Acetate Adhesive Applied from Solvent. Shear Strength of Assembly Developed at Room Temperature⁸⁸

prolonged, the strength falls again. It is of interest to note that DELMONTE states that the results so obtained were low compared with those obtained by complete evaporation of solvent followed by heat sealing.

A mathematical analysis of the stresses produced by the evaporation of solvent from a solution of an adhesive has been developed by JONES and MASLEM⁸⁸ in connection with work carried out on the performance of wire resistance strain gauges.

The slow solidification at atmospheric temperature of a mixture of catalysed monomer and powdered polymer or of partially polymerised monomer is comparable to the fusion and subsequent solidification of the molten polymer. Equally it should be capable of giving rise to relatively strain free bonds provided that the contraction which frequently occurs in the conversion of liquid monomer to solid polymer is not too great or can be counteracted by the addition of fillers. This system approaches one of the ideals which can be postulated, of a liquid adhesive which is a "potential solid" and to which solid state it can be converted at atmospheric

TABLE 23

SHEAR STRENGTH DATA FOR VARIOUS ADHESIVE-ADHEREND COMBINATIONS ^a

Adherend Adhesive	Cellulose nitrate	Polyvinyl acetate	Resor- cinol resin	Casein	Gum arabic	Rub- ber	Neo- prene
Stainless steel							
Shear strength (p.s.i.)	1580	2960	0	190	130	270	90
Standard error (p.s.i.)	29	44		29	16	18	4.5
Coefficient of variation (percent)	6.2	5.2		55	30	20	17
Number of specimens	11	12		12	6	9	11
Aluminium alloy							
Shear strength (p.s.i.)	1360	3560	0	120	^b 330	250	130
Standard error (p.s.i.)	32	65		12	^b 52	15	21
Coefficient of variation (percent)	8.0	8.8		28	^b 50	18	53
Number of specimens	12	23		8	^b 10	9	11
Paper-phenolic laminate							
Shear strength (p.s.i.)	^{cd} 1680	^{cc} 2480	^{cc} 1370	^c 1030	440	130	250
Standard error (p.s.i.)	31	93	28	30	24	5.5	6
Coefficient of variation (percent)	6.4	12	6.8	10	18	15	8.2
Number of specimens	12	10	11	12	11	12	12
Glass							
Shear strength (p.s.i.)	^{def} 1680	^{cdf} 2310	0	29	210	43	100
Standard error (p.s.i.)	42	110		6	7.1	3.5	14
Coefficient of variation (percent)	9.5	11		55	10	28	48
Number of specimens	14	6		8	9	12	11
Birch wood							
Shear strength (p.s.i.)	^c 1390	^{cc} 1990	^{cc} 1940	^{cc} 1660	630	160	180
Standard error (p.s.i.)	39	66	46	55	24	12	4.6
Coefficient of variation (percent)	9.3	10	9.7	11	13	26	8.9
Number of specimens	11	10	17	12	11	12	12
Hard rubber							
Shear strength (p.s.i.)	^{cd} 1000	^{cc} 630	^{cc} 590	150	240	190	230
Standard error (p.s.i.)	18	44	61	9.6	13	7	8.9
Coefficient of variation (percent)	6.3	22	23	21	18	13	13
Number of specimens	12	10	5	12	12	12	12

^a A double-lap tensile-type specimen with an overlap of 1 inch was used unless otherwise stated. ^b Specimens dried for 20 days instead of 7 days gave the following results: shear strength (p.s.i.), 530; standard error (p.s.i.), 68; coefficient of variation (percent), 43; and number of specimens, 11. ^c Specimens failed partly in adherend. ^d Overlap 0.4 inch or less. ^e Overlap 0.5 inch. ^f Compression shear.

TABLE 24

TENSILE-ADHESION STRENGTH DATA FOR VARIOUS ADHESIVE-ADHEREND COMBINATIONS ^a

Adherend Adhesive	Cellu- lose nitrate	Poly- vinyl acetate	Resor- cinol resin	Casein	Gum arabic	Rub- ber	Neo- prene
Stainless steel							
Tensile adhesion strength (p.s.i.)	2180	3600	0	510	110	260	170
Standard error (p.s.i.)	66	72		31	6	17	9
Coefficient of variation (percent)	10	10		21	19	23	16
Number of specimens	12	25	25	12	1	12	9
Aluminium alloy							
Tensile adhesion strength (p.s.i.)	1500	3270	0	110	110	390	290
Standard error (p.s.i.)	100	59		9.5	7	26	9
Coefficient of variation (percent)	23	9		30	18	23	10
Number of specimens	12	25	17	12	9	12	12
Paper-phenolic laminate							
Tensile adhesion strength (p.s.i.)	bc 860	bc 1060	b 830	bc 690	630	160	170
Standard error (p.s.i.)	110	75	52	37	42	15	9
Coefficient of variation (percent)	40	23	19	18	21	31	17
Number of specimens	10	10	9	11	10	10	12
Glass							
Tensile adhesion strength (p.s.i.)	bc 1040	bc 2430	0	0	260	34	90
Standard error (p.s.i.)	230	170			17	5	12
Coefficient of variation (percent)	60	16			21	47	46
Number of specimens	7	5	13	6	10	10	11
Birch wood							
Tensile adhesion strength (p.s.i.)	bd 1100	bd 960	bd 1180	bd 1020	d 400	d 170	d 340
Standard error (p.s.i.)	66	39	42	16	15	45	13
Coefficient of variation (percent)	19	14	14	5.3	12	26	12
Number of specimens	10	12	16	8	9	9	10
Hard Rubber							
Tensile adhesion strength (p.s.i.)	c 590	400	b 1340	130	320	130	240
Standard error (p.s.i.)	50	26	50	4	32	18	7
Coefficient of variation (percent)	27	20	12	11	31	44	12
Number of specimens	10	9	10	10	10	10	18

^a A specimen with a contact area of 1 square inch was used unless otherwise stated.
^b Specimens failed partly in adhesion. ^c Contact area 0.25 square inch. ^d Contact area 0.5 square inch.

temperatures, with minimum contraction during solidification and with the evolution of no volatile material.

(c) Performance and Applications of Thermoplastic Adhesives

As solutions in suitable organic solvents, thermoplastic adhesives are commonly used for sticking together, wood, leather, porcelain, glass, etc., and the literature is replete with a wide variety of formulations for solutions of this kind. These mixtures have the advantages of setting cold, under essentially neutral conditions, and unlike the thermosetting materials of being able to be used without specialised equipment.

The use of thermoplastic adhesives in highly stressed structures is relatively uncommon particularly as they have been found to fail at relatively light loads when long time-load tests have been carried out. Consequently their performances under standard and specified conditions are much less frequently examined than those of the thermosetting types.

Comparative figures for double lap shear strengths (see Chapter 9) of various adhesive-adherend combinations are given in Table 23⁸⁹. All the adhesives were applied in liquid or solution form and the surfaces of the adherends given an appropriate pre-treatment before coating and assembly.

It will be seen that in all cases examined, the two thermoplastic adhesives gave excellent comparative results. It must be added however that comparative long time-load tests showed the superiority of the thermosetting adhesive over the thermoplastic for supporting structural loads. The authors state that "the resorcinol resin showed no appreciable flow on supporting a load of 680 p.s.i. for 6 months without failure, whereas the polyvinyl acetate failed in 45 days under a load of 200 p.s.i."

Results obtained by the same authors for tensile strength are shown in Table 24.

Heat sealing of containers with polyvinyl acetate has been described by ROBINSON who used mixtures of polyvinyl acetate and dammar gum, or polyvinyl acetate and pentaerythrityl abietate^{90, 91}. The constituents were melted together and applied at 150–230° F to the container material. On solidification a seal was obtained which did not open up when the container was subsequently dipped in hot paraffin wax. Another mixture used for the same purpose consisted of 60% polyvinyl acetate and 40% pinewood pitch⁹².

Polymethyl methacrylate sheet lends itself admirably to fabrication by heat welding techniques. DELMONTE⁹³ claims that sheets bonded in this way have strength values approximately those of the original sheet and

that in addition the weld remains clear. He recommends a specific technique in which the surfaces to be welded are first heated until some localised decomposition occurs. The parts are then pressed together so that any excess molten material is squeezed out at the glue line, and can be removed by sanding after it has cooled and solidified.

The technique of using catalysed monomer or partially polymerised monomer for bonding the appropriate polymer has been successfully applied to vinyl and methacrylate resins. Monomeric methacrylic acid ⁹⁴ or the monomer of methyl methacrylate containing 0.01–1 % benzoin as catalyst have been suggested ⁹⁵ for cementing polymethyl methacrylate sheets. Wood, metal and other non-porous adhesives have been bonded by applying partially polymerised polyvinyl acetate and allowing the polymerisation to be completed *in situ* ⁹⁶.

Most types of thermoplastic adhesives in sheet form have been tested for suitability as the interlayer in laminated or safety glass. Originally celluloid was used but was found to discolour on prolonged exposure to sunlight, and was later replaced by cellulose acetate, plasticized by dibutyl phthlate. The use of either of these materials necessitates sealing the edges of the glass laminate with bitumen, to prevent the ingress of moisture and the risk of de-lamination. For sticking the interlayer to the glass, adhesives based on vinyl resins, acrylic resins and cellulose esters have all been used both alone and in various combinations.

These materials have now been replaced almost entirely by polyvinyl butyral sheet compounded with 20–30 % plasticizer. The use of a vinyl type interlayer has the advantage of not becoming brittle at temperatures as low as –40° F and of retaining its tensile strength at temperatures up to 120° F. Using equivalent thicknesses it gives a glass about five times stronger than when cellulose acetate is used. No separate adhesive is required to cement the interlayer to the glass and most important from a manufacturing point of view—no edge sealing is necessary.

Large quantities of cellulose nitrate adhesives are being used in the shoe industry, particularly in U.S.A., for cementing the soles to the uppers. The process has been described by ESSELEN ⁹⁷ and entirely eliminates nailing or sewing when the sole is attached. A measured quantity of the adhesive is applied to the sole and the bottom of the upper and allowed to dry. When the two parts are ready to be combined, the dry cement is moistened again with solvent and the parts brought into contact. Using specially prepared quick-setting cellulose nitrate adhesives, the sole and the upper need only be maintained in contact for less than 1 minute for satisfactory adhesion to occur.

It has been estimated⁹⁸ that in 1932 about 26½ million pairs of shoes were cemented in this way, requiring 100,000 gallons of nitro-cellulose cement and that by 1941 the number had increased to 61 million pairs—a striking example of how the success of an adhesive increases the demand.

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5D. ASPHALTIC BITUMEN

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§ 1. INTRODUCTION

(a) *Definition*

Asphaltic bitumen is generally a dark substance, consisting mainly of carbon and hydrogen and, further, of relatively small amounts of sulphur, oxygen, nitrogen, etc. It is a thermoplastic material; at ambient temperatures it is highly viscous to almost solid; by heating it to high temperatures it can be reduced to a low viscous condition. It is completely soluble in carbon disulphide.

By far the largest amount of the bitumen produced is obtained from crude mineral oils, from which the more volatile fractions (petroleum spirit, kerosine, lubricating oil) have been removed by distillation or extraction. In a number of cases chemical processes are used, particularly oxidation (blowing), to influence the properties of the final product.

Sometimes native asphaltic bitumens are used, in which case the natural consistency of the mineral product obviates the necessity of hardening by artificial means. They are often found associated with inorganic materials (native asphalts).

There is no great difference between processed and native bitumens and in the following pages no distinction will be made between these two types.

Apart from pure asphaltic bitumens, bituminous adhesives are sometimes made by compounding asphaltic bitumen with inorganic fillers or with organic materials like rubber, sulphurized or blown vegetable oils, etc.

There are a large number of allied substances, like coal tar pitch and other pitches, which likewise serve as adhesives. Generally speaking, their behaviour is subservient to the same laws which govern that of asphaltic bitumen, but, for the sake of brevity, this Chapter will deal mainly with asphaltic bitumen and only an occasional reference will be made to these other substances. For further information the reader is referred to ABRAHAM's handbook, *Asphalt and Allied Substances*¹.

(b) *Composition and Structure of Asphaltic Bitumen*

Both the composition and the structure of asphaltic bitumen are of a complicated nature. As it is outside the scope of this book to deal with this subject in detail, only its main outlines will now be considered.

Asphaltic bitumen, being a residual fraction of crude mineral oil, consists of a mixture of substances of relatively high molecular weight. Apart from small amounts of sulphur, oxygen and nitrogen, the material consists of carbon and hydrogen. These two elements are present in the form of aliphatic, naphthenic and aromatic groups; most of the molecules of the material contain more than one of these basic groups.

This complexity of the material means that bitumen cannot be broken down into its simple constituents. All existing methods of separation only produce fractions in which components are more or less concentrated according to a certain property. The study of the properties of such fractions has nonetheless provided a background from which a picture can be built up of the relation between the structure and composition of asphaltic bitumen.

Two main factors have to be considered: molecular size and degree of aromaticity.

Separation according to molecular size can be effected by dilution of the bitumen with an excess of low-boiling saturated hydrocarbons, ethers etc. Under these circumstances the bitumen is separated into a soluble oily fraction (maltenes) and an insoluble solid fraction (asphaltenes). The quantity and nature of these components vary with the conditions of precipitation.

The maltenes consist of hydrocarbons of an average molecular weight of, e.g., $0.5-1 \cdot 10^3$, the asphaltenes of hydrocarbons of much higher molecular weight. In the latter case, the results of different techniques employed for determination differ considerably; values of $5-100 \cdot 10^3$ may, however, be taken as the order of magnitude. This high value concords with the rheological character of bitumens, which character is typical of a colloidal system.

The quantity of asphaltenes obtained from bitumens of different origin or made by different methods of production, varies considerably; some bitumens contain only negligible quantities of asphaltenes; in most bitumens the amount ranges from 10–35%; for some very hard bitumens this figure is 50% and even higher.

The simplest way of expressing the degree of aromaticity is by means of the carbon-hydrogen ratio (C/H ratio). This ratio is lower for maltenes

than for asphaltenes from the same bitumen. Maltenes show atomic C/H ratios varying between about 0.6–0.9, asphaltenes in most cases between 0.8–1.2, depending upon the origin and the method of production of the bitumen.

The solubility of asphaltenes in maltenes depends primarily upon the difference in their C/H ratios. Qualitatively, it can be said that there is complete solubility when this difference is small; systems of a sol character exist under this condition. Conversely, solubility is slight when the difference in C/H ratio is substantial. In between these extremes, asphaltenes with a C/H ratio of 0.8–1.0 produce systems having the character of a gel.

This gel character follows from the rheological properties to be discussed further on and from the fact that an oil phase may be extracted from this type of bitumen by porous materials with which it is in close contact.

Sol-type bitumens do not exhibit this extraction; they can only bleed integrally into porous materials at high temperatures.

Further study shows that adsorption equilibria exist in asphaltic bitumens between asphaltenes and maltene fractions; it has been shown that at ambient temperatures the micellar phase consists of the asphaltenes and part of the maltenes.

For a fuller description of the structure and properties of asphaltic bitumen the reader is referred to PFEIFFER, *The Properties of Asphaltic Bitumen, with Reference to its Technical Applications*². In this book particulars are also given of the properties and applications of bitumen which may supplement the information given in the following pages.

(c) *Asphaltic Bitumen as an Adhesive*

Asphaltic bitumen finds widespread use as an adhesive. Examples are its various applications in the paper and timber industries, its use in road construction, where stone or sand is bound into a coherent mass, and its use for similar reasons in coal briquetting.

The use of asphaltic bitumen as an adhesive is primarily in virtue of its adhesive and mechanical properties, and also in most cases on account of properties such as its almost negligible permeability to water and its indifference to most chemicals. Further, its low price as compared with most other adhesives is often a decisive factor in favour of its application.

Generally speaking, given the right conditions (clean and dry surface of the substratum, low initial viscosity of the adhesive), asphaltic bitumen adheres well to other substances.

Mechanical properties are of significance in two respects. So that it can be applied to the substratum, the product must be of low viscosity; this

can be obtained either by heating ("melting") the bitumen, by dissolving it in volatile solvents of low viscosity or by emulsifying it in water. The circumstances under which adhesives are expected to do their ultimate job are not always the same and may necessitate adapting the hardness and elasticity of the bitumen to the specific requirements of the case. This can be effected within wide limits. The ultimate choice of the kind of bitumen most suitable for a given application depends upon the mechanical properties desired.

Water permeability is not a factor calling for extensive consideration in connection with the use of bitumen as an adhesive. It need only be said that the permeability to water of asphaltic bitumens is low ³ ($D =$ about 10^{-8} g/cm, mm Hg, h), most other materials showing appreciably higher values ⁴.

As regards resistance to chemicals, the main thing is that bitumen used as an adhesive should be resistant to oxidation. This oxidation of bitumen may cause some hardening and once again the prevailing conditions during both processing and ultimate use have to be considered. Hardening during processing can easily be compensated for by the use of a correspondingly softer bitumen; hardening during ultimate use is generally within acceptable limits.

Owing to its inert chemical character, bitumen has no chemical effect upon the substratum.

(d) *Characterisation of Bitumens*

The normal characterisation of bitumens by means of a routine analysis is mainly of a rheological nature, supplemented by some figures relating to composition.

In the following pages bitumens will be mainly described by two points of their viscosity (consistency)-temperature curve. This viscosity-temperature relationship shows little - if any - dependence upon the thermal history of the material. The two points referred to are the Ring and Ball softening point and the penetration at 25° C.

The Ring and Ball softening point ⁵ is determined by gradually heating in a liquid bath a ring filled with the bitumen and loaded by a ball and recording the temperature at which the bitumen has sagged a certain distance. It has been found that at this temperature the viscosity is about $1-2 \cdot 10^4$ poises ². It may be said that the Ring and Ball softening point represents the equiviscous temperature for this viscosity.

The penetration ⁶ is determined by means of a loaded needle, which penetrates into the bitumen for a fixed time at constant temperature (here

25° C). Comparison of penetration measurements with determinations of the absolute viscosity and the elasticity of bitumens has given a reliable basis for the interpretation of the results of this test ².

Both determinations have been accurately standardised.

§ 2. PROPERTIES OF ASPHALTIC BITUMEN

(a) *Adhesion*

It was shown in Chapter 2, dealing with adhesion generally, that our fundamental understanding of this phenomenon is still limited, particularly where the more complicated materials are concerned. Correlations may exist in a number of cases between properties like the VAN DER WAALS constant, the dipole moment, the parachor, the energy density, the dielectric constant, on the one hand, and phenomenological constants of adhesion, on the other, but a quantitative relation is still far from having been established.

The discussion of the adhesive aspects of asphaltic bitumen in this Chapter, therefore, can scarcely be otherwise than mainly from a phenomenological angle, because our knowledge of the composition pertains to its average composition, or that of important parts of it, rather than to the presence of special groups of atoms, like those of a strong dipole nature, which may have a distinct influence upon the phenomena of adhesion.

The adhesion of asphaltic bitumen to other materials will now be discussed in the light of our present knowledge with reference to:

- (i) The surface tension of the bitumen.
- (ii) The contact angle, or the adhesion tension, with respect to the substratum.

Some additional facts respecting the practical side of adhesion will be given in § 3 of this Chapter.

When bitumen used as an adhesive is in the presence of water, which it sometimes is, allowance has to be made for the interfacial tension between it and water, as also for the contact angle in the bitumen-water-substratum system.

(i) *Surface Tension*

The surface tension of asphaltic bitumen depends little upon its hardness or type; at a rough approximation, the following formula ⁷ expresses its relation to temperature:

$$\gamma_{LG} = 50 - 0.056 T \text{ erg/sq.cm} \quad (1)$$

in which T is the temperature in °K.

This low value of the surface tension implies that the addition of other substances to bitumen will seldom change its surface tension appreciably.

The interfacial tension of bitumen against water is much more dependent upon its composition. Commercial bitumens mostly show values of 25–40 erg/sq.cm^{7, 8}, but the addition of substances possessing capillary activity may reduce the interfacial tension to 5 erg/sq.cm or less⁹.

(ii) *Contact Angle*

In the absence of water, the contact angle of bitumen upon virtually every substratum is small. The receding contact angle is usually 0°; the advancing contact angle may vary from 0° to *e.g.* 45°. The mechanical forces applied during processing (coating, mixing) to overcome the viscous resistance of the adhesive are sufficient to obtain easily a complete covering of the substratum by the bitumen.

In the presence of water, the contact angle of bitumen may be higher. The effect in actual practice is mainly manifested if the viscosity of the bitumen is low.

The receding contact angle largely depends on the nature of the substratum; on metals it is generally small; it may be large on stone material, especially if bituminous products of low viscosity are used and water has access to them shortly after processing. Under these circumstances, values may be recorded of 90°, and even higher, for the bitumen-water-stone system.

This stripping is less marked from stones of an alkaline character than from acidic materials, one of the reasons probably being the presence of high molecular weight acids in the bitumen. The receding contact angle in this initial period of contact between bitumen and stone in the presence of water can be considerably reduced by the addition of suitable capillary-active substances to the bitumen *e.g.* of high molecular amines in the case of acid stones or by chemical treatment of the surface of the stone, *e.g.* by iron salts.

After somewhat longer contact between the bitumen and the substratum, the receding contact angle in the presence of water is usually small enough to be considered negligible.

The advancing contact angle of bitumen over wet surfaces is often large. In these cases it is impossible to coat a wet surface with pure bitumen adequately and it has been necessary to devise special processes for the purpose, in which capillary-active substances again play an important part. Materials similar in character to bitumen are less troublesome to coat with pure bitumen in the presence of water (coal briquetting).

A substratum can be reliably wetted by bitumen in the presence of water by using bitumen emulsions. In this case the bitumen can adhere during the coagulation process, initiated by evaporation of the water or by the action of coagulating ions.

(b) *Rheology*

We saw in Chapter 3 that there are three periods in the use of adhesives, the rheology of the adhesive playing a different part during the application, hardening and final use of the adhesive.

The following will therefore be considered individually.

- (i) The rheology during the application of the adhesive, that is before hardening.
- (ii) The rheology during hardening; in this phase the surfaces are joined.
- (iii) The rheology of the hardened layers.

(i) *Rheology before Hardening*

The low viscosity necessary for processing adhesives can be obtained with bitumen in three different ways:

- (1) By heating ("melting").
- (2) By dissolving in solvents of low viscosity and suitable volatility.
- (3) By dispersing in water.

(1) When heated, bitumens, being thermoplastic materials, gradually soften from a semi-solid to a fluid state; within the limits of their thermal stability the range of viscosities desired for processing can always be reached.

In the range of processing temperatures the dependence of viscosity on temperature can be described by WALTHER's formula¹⁰:

$$\log \log(\nu + 0.8) = -m \log T + C \quad (2)$$

in which ν = kinematic viscosity in cS and T = temperature in °K.

The values of the constants m and C and, therefore, the temperature at which a certain viscosity is reached, depend upon the hardness (penetration) and the composition of the material.

Examples of viscosities of bitumens are given in Table 25. The viscosity data are here expressed as equiviscous temperatures.

The viscosity needed when applying the fluid adhesive varies with the type of application. The order of magnitude of this viscosity amounts to 10^2 – 10^3 cS for brushing, spraying, or dipping, and 10^3 – 10^4 cS for spreading by means of an application roller and doctor knife. To obtain satisfactory contact, the bitumen must penetrate to some extent into pores etc. of the substratum, but this penetration must be within certain limits, especially in cases where the substratum consists of thin sheets like paper.

TABLE 25
EQUIVISCIOUS TEMPERATURES OF VARIOUS BITUMENS

Bitumen		Temperature in °C at which the viscosity of the bitumen amounts to:			
R & B soft. point °C	Penetration/25° C	10 ² cS	10 ³ cS	10 ⁴ cS	10 ⁵ cS
Borneo bitumens					
38½	145	117	88	68	54
54½	14	137	105	83	68
Venezuelan bitumens					
Normal residual grades					
33	350	144	99	70	49
39	190	154	107	77	56
46	90	167	117	87	65
55	45	179	129	97	76
62	25	191	140	107	88
70	15	198	150	118	97
Hard residual grades					
85	10	224	166	128	101
115	4	267	204	164	135
125	3	287	224	185	156
Blown grades					
85	40	220	168	134	109
85	25	225	173	139	115
115	15	258	208	175	151

(2) Any viscosity desired for cold processing can be reached by dissolving bitumens in volatile solvents of low viscosity. Normally petroleum distillates are used; the order of magnitude of the concentrations is 50% by volume.

Intermediate degrees of dilution, with corresponding temperatures of heating, are also employed (cutbacks).

(3) In the case of bituminous emulsions there are two types to be considered *viz.*, soap emulsions and clay emulsions.

In the first case soaps are used as the emulsifier and the emulsions show virtually Newtonian flow for concentrations up to about 60% by vol. of bitumen, with viscosities up to about 10² cS.

In the second case clay is used as the emulsifier in amounts of, *e.g.*, *circa* 4% by wt. (1.5% by vol.) relative to the bitumen; the bitumen concentration of such emulsions is also up to about 60% by vol. The rheological nature of these emulsions is quite different from that of soap emulsions. They possess a marked yield stress and are thixotropic and can therefore be applied in thick layers on vertical walls, *e.g.* as an adhesive for tiles.

(ii) *Rheology during Hardening*

The changes in the viscosity after application of the layer of the bituminous adhesive will also be discussed for the three different ways of processing.

(1) After hot application the bitumen will gradually cool down and increase in viscosity.

The adherends are joined during this period. The viscosity at this moment varies in different applications: *e.g.*, the viscosity during compaction of bitumen-coated aggregates amounts to 10^3 – 10^5 cS.

After the adherends have been joined, no undue deformation should occur in the final object. The viscosity at which the object becomes rigid enough will depend upon the stresses brought to bear upon the bitumen layer or the bitumen joint and upon the time. The Ring and Ball softening point of the bitumen, at which the viscosity is about 10^6 cS.¹¹, may often approximate this condition.

There will be some shrinkage while the material is cooling; for all bitumens a value of 0.00061 per °C can be taken as the cubic coefficient of expansion¹².

(2) Solutions of asphaltic bitumen will increase in viscosity by loss of solvent. No general simple formula can be given for the relationship between viscosity and concentration. For concentrations up to 80 % by vol. of bitumen the formula

$$\eta_r = \left(\frac{1}{1-c} \right)^n \quad (3)$$

applies, in which η_r is the viscosity ratio, c the concentration and n a constant, depending on the type of solvent and bitumen.

The shrinkage in this case is equal to the volume concentration of the solvent.

(3) The viscosity characteristics of emulsions during coagulation are not simple. There will be a rather sudden increase in viscosity at the moment when coagulation has progressed to the point where a continuous bitumen film begins to be formed.

Shrinkage will again be equal to the volume concentration of the water.

Both solutions and emulsions of asphaltic bitumen can only be applied as an adhesive if the diluting agent can be eradicated by absorption in pores or diffusion through voids of the adherends.

(iii) *Rheology of the Hardened Layers*

After complete hardening, little difference exists between layers formed by

hot or by cold application, except when clay emulsions have been used (see p. 257).

Whereas in the heated or dissolved state bitumens behave nearly enough like a Newtonian material, only a limited group of undiluted bitumens do so at normal temperatures. Depending upon the composition, elastic and thixotropic effects generally accompany permanent deformation¹³.

In this section we shall only discuss deformations of a completely or partly permanent type (viscous or visco-elastic deformations). Completely elastic deformations will be discussed in the next section.

In relation to the viscous or visco-elastic type of deformation bitumens are usually divided into three groups.

The first group comprises bitumens that behave entirely, or almost entirely like Newtonian liquids. The rate of deformation is proportional to the stress applied. Elastic effects are negligible, thixotropy is absent.

The second group comprises bitumens exhibiting distinct elastic effects which strongly influence their performance in many applications. After the initial stage of deformation, the rate of deformation of these bitumens is virtually proportional to the stress. Thixotropic effects are negligible.

The third group comprises bitumens which show almost complete elastic resilience after relatively slight deformation (shear $< 0.1-1$, depending upon stress and time.) With greater deformation the elastic resilience is no longer complete. The rate of permanent deformation increases more than proportionately with the stress. The elastic effects are greater than in the second group and thixotropy is considerable.

This third group is formed by the gel-type bitumens mentioned in Section 1, (b) of this Chapter, whereas sol-type bitumens make up the first and second groups. Bitumens free from asphaltenes always belong to the first group.

Bitumens of the third group are in most cases manufactured by a chemical process, *i.e.* by oxidation, whereas the bitumens of the two other groups are mostly prepared by some form of distillation (or sometimes by an extraction process), if necessary accompanied by a degree of blowing (semi-blown bitumens).

For a given Ring and Ball softening point the penetration at 25° C of bitumens of the third group is highest and that of the first group lowest. This is mainly due to the influence of the elastic effects on the penetration determination¹⁴.

Each group contains bitumens of various hardnesses. The examples given in Table 25 comprise representatives of these three groups and it can be seen that variations occur in Ring and Ball softening points over a

range of about 100° C and in penetrations at 25° C by a factor of about 100.

These three groups of bitumen will now be discussed separately in somewhat greater detail. A number of examples will be given of products from origins in different parts of the world, so that the picture will represent a survey of a wider range of products than normally commercially available in any particular country.

(1) Bitumens of the first group, being to all intents and purposes Newtonian in character, call for no special comment. Table 26 lists some facts relating to rheological properties as a function of temperature for a number of origins. The low resilience mentioned in a number of cases is independent of temperature.

TABLE 26

RHEOLOGICAL PROPERTIES OF BITUMENS OF THE FIRST GROUP

Origin	Process of Manufacture	R&B soft. point °C	Pen/ 25° C	Viscosity in poises at				Resilience in cm/cm after prolonged loading with a shearing stress (dn/cm²) of:			
				0° C	15° C	25° C	40° C				
								10²	10³	10⁴	10⁵
Borneo	dist. dist. and blowing	47	47	10¹¹	1.5 · 10⁸	4 · 10⁶	6 · 10⁴	0.00	0.00	0.00	0.00
Java		49	44	2 · 10¹⁰	7 · 10⁷	3 · 10⁶	8 · 10¹	0.001	0.01	0.05	0.09
California		48	54	10¹⁰	5 · 10⁷	2 · 10⁶	7 · 10¹	0.00	0.00	0.00	0.00
California	moderately cracked	19/	19/								
		85	50° C	—	—	8 · 10¹⁰	3 · 10⁸	—	0.01	0.02	0.10
Highly cracked material		51	36	—	3 · 10⁸	1.5 · 10⁷	1.3 · 10⁵	0.001	0.01	0.02	0.03

Viscosities above 10⁸ poises obtained by extrapolation.

The viscosities at ambient temperature of bitumens of this type can again be represented as a function of temperature by WALTHER's formula (2), given on p. 256¹⁵.

The relation between penetration and viscosity at the same temperature for this type of bitumens has been found to be:

$$\eta = \frac{1.58 \cdot 10^{10}}{\text{pen.}^{2.16}} \tag{4}$$

(viscosity in poises, pen. in 0.1 mm at 100 g load and 5 sec penetration time)¹⁵.

Pitches, e.g. coal tar pitch, often show a close resemblance to bitumens of the first group.

The above details provide all the information required to calculate rates of deformation under prolonged loading when bitumens of this type are applied as adhesives, if the stress distribution in the joints is known.

(2) Bitumens of the second group show both permanent deformation and distinct elastic effects under any stress applied for a given length of time.

The elastic effects consist of a fore-effect, *i.e.* a relatively high initial rate of deformation, and an after-effect, which consists either in resilience or in a gradual relaxation of stress ².

These properties can be represented qualitatively by a model system (Fig. 87) consisting of a VOIGT element and a viscous element in series ¹⁶.

Experimentally, the quantitative relationship of deformation to time for slight deformation under constant stress is found to be:

$$\gamma = \frac{\tau}{\eta} t + \tau a t^n \tag{5}$$

in which
 γ = deformation (shear)
 τ = shearing stress
 η = viscosity of bitumen (practically constant)
 n is a constant amounting to about 0.50; a depends upon the temperature ¹⁷.

This equation can be obtained for a model system by replacing the VOIGT element in Fig. 87 by an infinite series of VOIGT elements with different η_i/G_i ratios.

For considerable deformation the relationship is:

$$\gamma = \frac{\tau}{\eta} t + \gamma_m \frac{1}{1 + \gamma_m \frac{b}{\tau}} \tag{6}$$

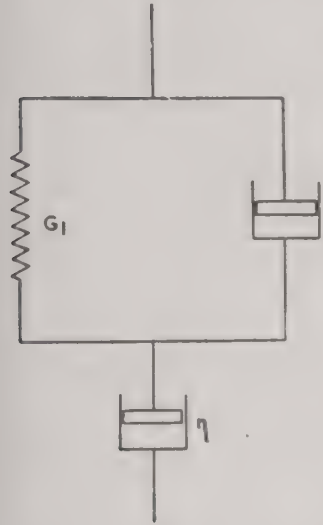


Fig. 87. Model system of a bitumen of the second group (elastic sol type).
Viscous element η
VOIGT element: viscous element η_1 + elastic element G_1 parallel coupled.

which shows that the elastic deformation approaches a constant final value with time approximating the value γ_m at high stresses ¹³. The constant b is of the order $50 \cdot 10^3$ dyne/sq.cm; γ_m normally varies between about 0.25 and 0.50. Both b and γ_m are almost indifferent to temperature up to the Ring and Ball softening point.

The visco-elastic effects of bitumen must be attributed to the presence of micelles of comparatively large particle size and ample deformability. This deformability must, however, be considered to be limited at high stresses because of the maximum elastic deformation of the bitumen as expressed by formula (6).

The course of the resilience after deformation of these bitumens is in line with that of the generalised model system ¹³; this means that the rate

TABLE 27
RHEOLOGICAL PROPERTIES OF BITUMENS OF THE SECOND GROUP

Origin	Process of Manufacture	R & B soft. point °C	Penetration at:				Viscosity in poises at: ¹					a · 10 ⁶ (c.g.s.) at:				n	γ_m	b · 10 ⁻³ (dn/sq. cm) at 25° C
			15°C 25°C 40°C 55°C				15° C	25° C	40° C	55° C	15° C	25° C	40° C	55° C				
			15° C	25° C	40° C	55° C												
Mexico Venezuela " "	dist.	57	19	46	164	—	—	2 · 10 ⁷	6 · 10 ⁵	3.3 · 10 ⁴	abt.	0.2	0.60	3.0	9.8	0.49	0.56	33
	"	38	69	195	—	—	2 · 10 ⁶	1.8 · 10 ⁵	10 ⁴	—	abt.	0.6	2.0	7.2	—	0.50	0.29	47
	"	55	17	44	185	—	1.5 · 10 ⁸	7 · 10 ⁶	1.9 · 10 ⁵	1.2 · 10 ⁴	abt.	0.2	0.59	3.1	9.8	0.50	0.40	47
	"	68	8	17	64	250	—	—	2 · 10 ⁷	10 ⁶	abt.	0.04	0.1	0.43	1.88	0.45	0.44	39

¹ In a number of cases approximate values owing to slight deviation from Newton's law.

of the resilience process is closely connected with that of the initial elastic deformation and decreases with increasing hardness of the bitumen when compared at the same deformation obtained under the same stress.

Data relating to various bitumens of this group are recorded in Table 27.

Further comparison between the penetration and the viscosity at the same temperature shows that the penetration is no longer a sufficient basis for a calculation of the viscosity. This is especially the case at low penetrations, where the elastic part of the deformation forms a considerable part of the total deformation in the penetration test. The actual viscosity, measured according to formulas (5) and (6), is higher than the viscosity calculated from the penetration by formula (4). At higher temperatures, when creep phenomena are more likely to be in evidence, the ratio may vary from 1–10, depending upon the degree of elasticity of the product. At lower temperature this ratio may even be appreciably higher.

When comparing bitumens of the first and second groups it may be found that the difference in viscosity is small relatively to that in penetration if this comparison is made at temperatures equally removed and not unduly different from the Ring and Ball softening point, hence in the temperature range within which creep phenomena are most likely to occur. Therefore, the permanent deformation under specific circumstances can roughly be taken as equal for bitumens of both types with the same Ring and Ball softening point. This can also be expressed by the rule that the permanent deformation under fixed conditions of stress is primarily governed by the difference between the Ring and Ball softening point and the temperature under consideration and not by the type of the bitumen. In the range of temperatures considered it can be taken at a very rough approximation that the viscosity varies by a factor 10^1 for every 10°C difference in temperature. It is evident from formula (2), however, that this factor increases at lower temperatures.

(3) Bitumens of the third group show complete elastic deformation under relatively small loads exerted for a limited length of time; with larger loads and longer times, part of the deformation is permanent.

In the first case it has been found that the retarded elastic deformation can be represented by

$$\gamma = \tau a t^n \quad (7)$$

in which n is a constant (about 0.4) and a depends upon the temperature¹⁷.

In the second case an experimental relation can be given as follows:

$$\gamma = \epsilon^m f(\tau) + \gamma_m \frac{1}{1 + \gamma_m \left(\frac{b}{\tau}\right)^{0.9}} \quad (8)$$

This equation shows that the permanent deformation is no longer always proportional to stress or time. The parameter m is a function of the stress applied; it differs little from 1 with small stresses, but increases with the stress and may then reach a value of, *e.g.*, 2 for a number of representatives of this group. γ_m in this case is larger than the corresponding magnitude of bitumens of the second group and often exceeds a value 1.

Formula (7) can be related to model systems in the same way as to bitumens of the second group, the main difference being that no viscous element η is incorporated in the model. The complicated nature of equation (8) makes it clear that the rheological properties of bitumens of the third group are no longer amenable to simple analysis. However, here again a practical rule exists for the flow in the high-temperature range of technical application, namely that the permanent deformation is often of the same order of magnitude as for other types of bitumen if the difference between Ring and Ball softening point and the temperature under consideration is the same.

Contrary to the case of bitumens of the second group, this rule is of only limited value as applied to bitumens of the third group, especially at low shearing stresses, when the gel structure of these bitumens is apt to cause a yield stress. The transition from flow to no flow, however, is much more gradual than in many other materials and it is hardly possible to give reliable figures even for the order of magnitude of this yield stress.

In Table 28 some data of rheological constants are given for various bitumens of the third group.

TABLE 28
RHEOLOGICAL PROPERTIES OF BITUMENS OF THE THIRD GROUP

Origin	Process of Manufacture	R & B soft. point °C	Penetration at:			a · 10 ⁶ (c.g.s.) at:				n	γ_m	b · 10 ⁻³ (dn/sq.cm) at 60° C
			25°C	40°C	60°C	25°C	40°C	60°C	85°C			
Mexico	blowing	90	23	53	158	0.06	0.25	1.95	12.4	0.39	1.2	6.8
Venezuela	„	90	21	48	150	0.04	0.19	1.06	10.1	0.41	1.1	9.6
Texas	„	88	27	62	180	0.03	0.13	1.23	6.6	0.39	1.1	12.6
Venezuela	„	87	35	75	205	0.08	0.41	2.14	20.0	0.42	1.1	3.9
Venezuela	„	119	14	27	64	—	abt. 0.01	abt. 0.07	0.50	0.41	1.4	49, 85° C

The three groups of bitumens may best be compared by plotting the ratio τ/γ against time, both on a logarithmic scale.

Straight lines, under a slope of 45°, are obtained with bitumens of the first group. With the second group the slope is smaller at short deformation

times. With the third group, one single curve is obtained for slight deformations only; but this ceases to be the case for larger deformations because the deformation for a fixed period is no longer proportional to the stress (formula (8)).

Curves are given in Figure 88 for various types of bitumen of different hardness.

These curves are valid at a temperature of 25° C. When considering creep phenomena at higher temperatures, approximate curves can be obtained by shifting the curves in Fig. 88 by the factor 10¹ mentioned before

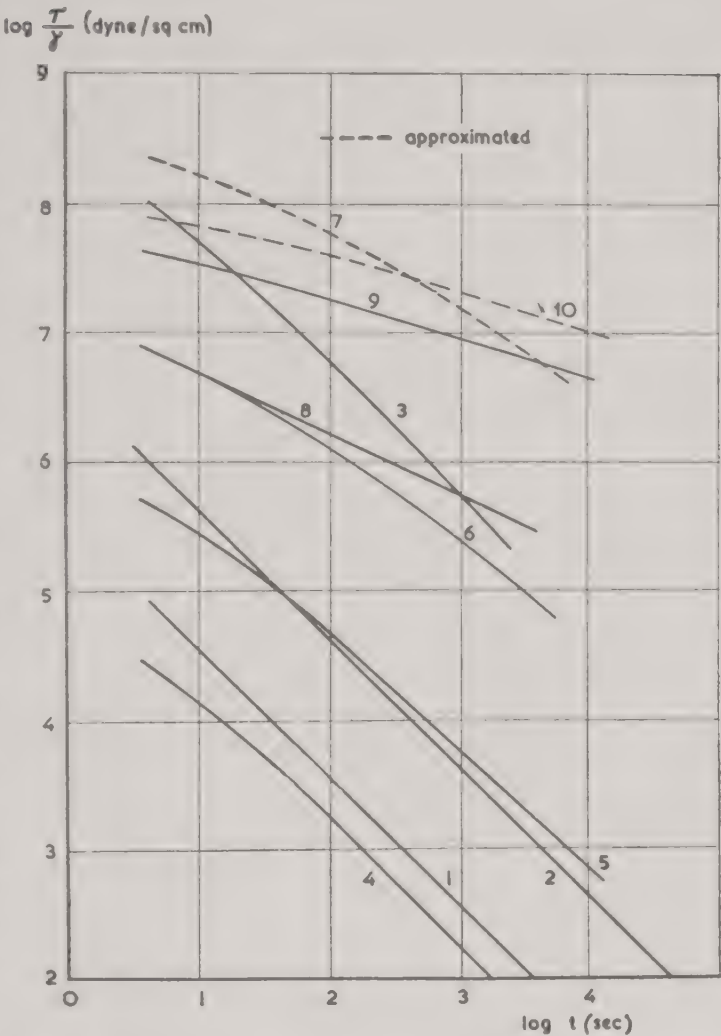


Fig. 88. Resistance to deformation (shearing stress/shear) at 25° C of various bitumens as a function of time during long periods of deformation.

No.	Group of bitumen	Origin	Process of manufacture	R & B °C	pen/25° C
1	1	Borneo	dist.	39	140
2	1	"	"	47	47
3	1	"	"	66	3
4	2	Venez.	"	38	200
5	2	"	"	55	44
6	2	"	"	67	15
7	2	"	"	114	3
8	3	"	blown	98	18
9	3	"	"	119	14
10	3	"	"	135	10

to lower deformation times for every 10°C increase in temperature above 25°C , with the same restriction as previously discussed.

The effect of an isotropic pressure besides the deviatoric state of stress upon asphaltic bitumens is quite considerable. A factor of 3–4 per 100 kg/sq.cm can be taken for bitumens of the first group and of 2–2.5 for the other bitumens. However, pressure on joints will seldom be high enough to change their viscosity characteristics to any appreciable extent.

(c) *Elasticity*

During rapid deformation, *e.g.* shocks, sudden bending etc., the permanent part of the deformation is negligibly small and the deformation can then often be considered as an elastic one. This means that the model system as given for bitumens of the first group (one viscous element) and for the second and the third group (VOIGT elements + viscous element, VOIGT elements only, respectively) does not completely represent the mechanical properties of the bitumen, but that a purely elastic element has still to be added (Fig. 89)^{16, 17}.

These models are qualitative representations of the transition of a purely elastic to a purely viscous, or retarded elastic character of the

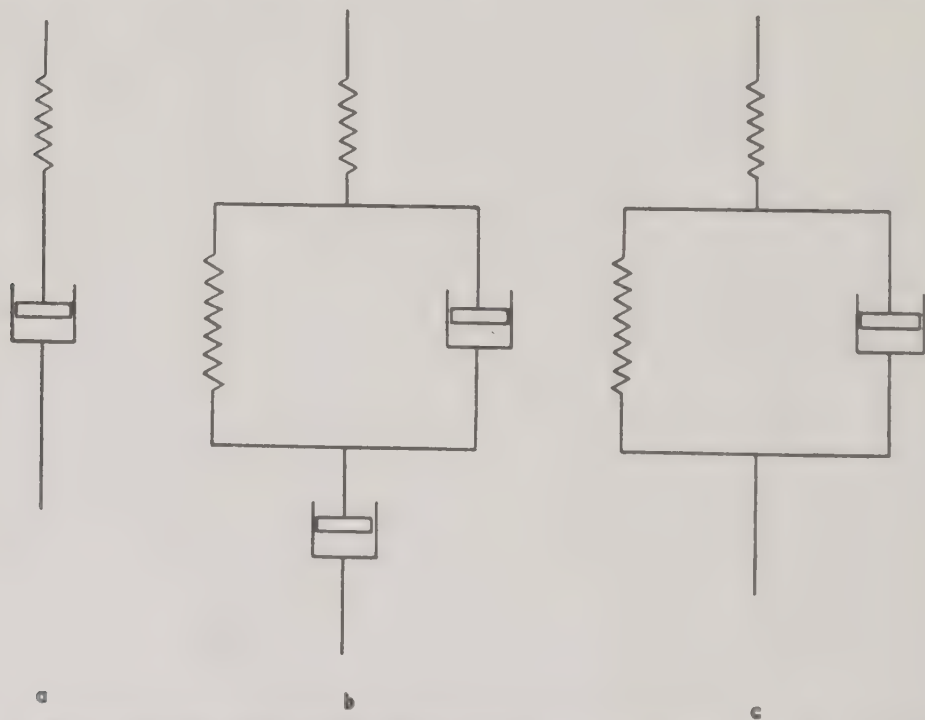


Fig. 89. Complete qualitative model systems of bitumens of the three different groups.

References p. 277

material. Quantitative representation can again be obtained by coupling in series an infinite number of VOIGT elements.

In infinitely rapid deformations, it is the elastic element only which determines the resistance to deformation (τ_y), which should, in this case, be described as an elasticity (shear) modulus. With less rapid deformations a number of VOIGT elements will also play a rôle, so that the resistance will then be smaller. The decrease in resistance will depend upon the distribution of VOIGT elements in the series.

The behaviour of bitumens of different hardness and type found in experiments¹⁸ is as shown in Fig. 90.

Not all the elastic parts of the curves of Fig. 90 have actually been determined; some of them have been approximated on the strength of general considerations to give a more complete, if only qualitative picture. In this way the representation of the mechanical properties of bitumens as given in Fig. 88 is complete for the full range of deformation times.

When considering elasticity phenomena at lower temperatures, the curves have again to be shifted; here, however, the factor 10^1 in time for every 10° C temperature difference from 25° C

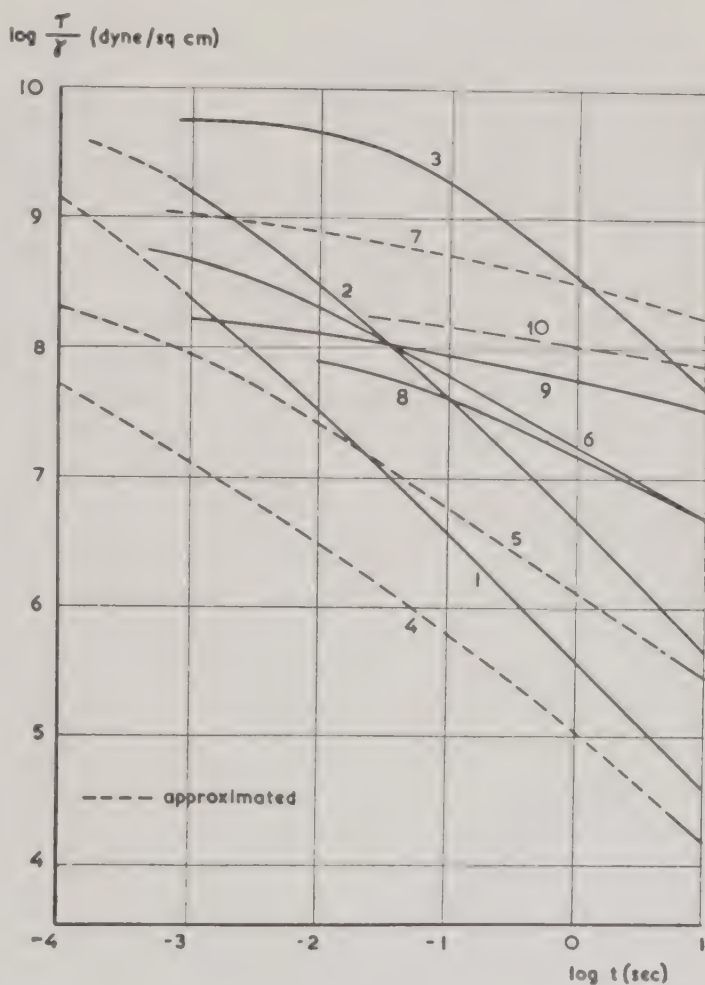


Fig. 90. Resistance to deformation (shearing stress/shear) at 25° C of various bitumens as a function of time during short periods of deformation. For characterization of the bitumens see Fig. 88.

is normally too low; for hard products the factor may amount to, say, $10^{1.5}$.

It has been found that the maximum value for the shear modulus amounts to about $5 \cdot 10^9$ dyne/ sq.cm ($5 \cdot 10^3$ kg/ sq.cm), the same value applying to pitches. This value is about 100 times lower than that of hard metals, etc.

It is useful to know for the calculation of Poisson's constant that the compressibility of bitumens is about $40 \cdot 10^{-6}$ sq.cm/kg, so that the reciprocal value is $25 \cdot 10^9$ dyne/sq.cm. For high values of the shear modulus G this value has to be taken into account in the calculation of the elasticity modulus E .

(d) *Breaking Strength*

Our present knowledge of the breaking strength of various bitumens is still far from complete. Some existing data¹⁸, however, show that the difference in tensile strength of bitumens of different hardness and type is comparatively small in relation to the substantial differences in resistance to deformation τ/γ as discussed in the preceding sections. The order of magnitude of the breaking strength can be taken as $20 \cdot 10^6$ dyne/sq.cm = 20 kg/ sq.cm. At the moment, this value is near enough to enable us to study the occurrence of fracture in bitumens. For other stress distributions the breaking strength may, however, be higher.

Apart from these more theoretical investigations, conventional tests are often applied to compare bitumens for breaking tendency. There are two distinct types of test, *viz.*,

(1) Relatively slow tests, the most common method being the FRAASS breaking point¹⁹. A metal plate covered with a thin layer of bitumen is slowly bent (for 10 sec.). The temperature during this test is continuously lowered and the bending experiment is carried out at regular intervals. The temperature at which cracks can be observed in the bitumen is the FRAASS breaking temperature. The penetration at this temperature is often between 1–2 for bitumens of the first and second groups and somewhat higher for bitumens of the third group.

(2) Rapid tests, of which an example is the Ball Drop Test²⁰. The weight is noted of the ball which, falling from a given height, causes fracture. At the same penetration at test temperature, the shatter resistance increases from bitumens of the first, to bitumens of the third group; even more so, if bitumens of the same Ring and Ball softening point are compared at the same temperature.

On account of the comparatively slight differences in breaking strength

between various bitumens, both groups of test determine the resistance to deformation or the modulus of elasticity, rather than the strength.

(e) *Durability*

After the application of an adhesive for cementing purposes, its properties should not change appreciably as time goes on. At this point we would do well to consider two agencies liable to induce changes in bitumens, namely:

- (a) Water during prolonged immersion.
- (b) Oxygen, especially in the absence of light.

(i) *Influence of Water*

Water may be absorbed in bitumen if the latter contains small amounts of water-soluble components, traces of salt in particular, which it normally does. By a kind of osmotic process the water diffuses into the bitumen and dissolves the salt, producing small globules of water in the bitumen. Relatively large amounts of water can therefore only be absorbed if the surrounding water is more or less pure.

It has been found that water absorption only causes perceptible changes in the mechanical properties of bitumen which is exposed in its applied form to high temperatures for long periods (years). This is because the diffusion process is very slow, owing to the scant molecular solubility of water in bitumen and the low diffusion constant in this highly viscous medium.

Thus water absorption only becomes a factor in exceptional cases, namely in conjunction with water-permeable or porous adherends in continuous and very prolonged contact with pure water at high temperatures.

(ii) *Influence of Oxygen*

The influence of oxygen on the durability of asphaltic bitumens may be somewhat more serious. In the oxidation of asphaltic bitumen, there are two distinct types of process, which may eventually change its properties, namely photochemical oxidation and oxidation in the absence of light. The latter type will have to be considered as it affects bitumen used as an adhesive.

The same factors which induce water absorption favour this oxidation process, *viz.*, accessibility to the agent, high temperature, low viscosity of the bitumen. In extreme cases in practice, the bitumen hardens, sometimes to the point of a decline in penetration by, *e.g.*, a factor 2 in one year.

Normally, however, the increase in hardness is much less, as the accessibility to oxygen, the temperature or the penetration of the bitumen into the cemented object is in most applications appreciably lower than in this extreme case.

In most cases there is no objection to some degree of hardening, because a certain amount of change in properties at low temperatures has been allowed for in the choice of bitumen made.

In other cases even a high degree of hardening may be permissible, as, for example, in that of bituminous laminated paper. True, there should be no appreciable hardening before the paper is used as wrapping material, but there is unlikely to be any at that stage, since oxygen can have but limited access to paper stored in rolls. Once the paper is in use as wrapping, it will matter little if the bitumen does harden because, if properly used, the wrapping is not subjected to major deformation.

(f) *Influence of Fillers, etc.*

In applications of asphaltic bitumen as an adhesive, other materials are sometimes added to the bitumen in order to change its properties, to reduce the costs, etc.

These auxiliaries fall into two groups, *viz.*

- (a) Those which form a separate phase in the bitumen (inorganic fillers and certain organic materials).
- (b) Those which dissolve in the bitumen.

Examples of the first group are limestone, cement, quartz and other fillers, the clay skeleton of layers formed from clay emulsions and rubber.

An example of the second group is provided by polymerized fatty oils. In this case an unblown or partly blown oil is added to the bituminous material and the mixture is sulphurized or oxidized.

We shall briefly consider how these auxiliaries affect the properties of the material.

Adhesion, considered as an interfacial phenomenon, is not impaired by these admixtures, as the structure of the interface is not changed to its disadvantage. Improvements of "adhesion", as sometimes reported, are usually attributable to changes in the mechanical characteristics of the material.

Rheological properties may undergo considerable modification as the result of the addition of these substances.

Normal iso-dimensional mineral fillers in amounts up to about 25% by vol. increase the viscosity of the material over the whole range of temperature by approximately the same factor, the latter depending upon

the amount of filler. They do not change the type of the material and, roughly speaking, the result is an increase in equiviscous temperature. This increase is about 4°C for 10% and 15°C for 20% by vol. of filler.

In higher concentrations the filler may form some skeleton in the material and thus induce a yield stress ²¹.

Effects of the same nature can be obtained with smaller amounts of flake type and especially of fibrous fillers.

As long as no yield stress is induced by the filler, no considerable differences in processing conditions and creep phenomena exist between a pure bitumen and a bitumen-filler mixture of equal Ring and Ball softening point. If, however, in high concentrations a yield stress is induced in the material, the conditions become more complicated and depend upon the characteristics of the filling material.

A yield stress is also induced in dried clay emulsions of bitumen by a clay skeleton, so that even with soft bitumens no flow occurs in applications to, *e.g.*, vertical walls. If, however, the material is subjected to deformation of some magnitude, the skeleton is destroyed once and for all.

Rubber can be incorporated in bitumen either by using mixtures of bitumen emulsion and latex, or by adding powdered rubber to the bitumen. In course of time the rubber swells to approximately five times its original volume, extracting components of lower molecular weight from the bitumen ²², owing to which the bitumen phase hardens. With relatively small amounts (up to 5%), the swollen rubber particles then only increase the visco-elastic effects as compared with those of the original bitumen; with larger amounts, the rubber particles form to some extent a continuous structure in the bitumen and the properties of the material are changed in the direction of a yield stress.

The incorporation of polymerized fatty oils may increase the visco-elastic properties of bitumens considerably; at the same time a more definite yield stress may result. The addition of these oils is at present the best means of obtaining bitumen of maximum elastic character.

The incorporation of rubber or polymerized fatty oils may entail certain restrictions in the processing conditions, because of the lower heat stability of these materials as compared to that of bitumen.

Changes are also observed in the elasticity discussed on p. 266 when bitumen is mixed with other materials. Upon the addition of inorganic fillers, the elasticity modulus changes according to a rather complicated mixing rule ¹⁸; as these fillers have a higher modulus, the modulus of the mixture increases as compared to that of the pure bitumens.

With rubber, the effect of the hardening of the bitumen phase by the

swelling of the rubber particles is counteracted by the presence of very soft rubbery particles; no conclusive data are available as to the final result.

The presence of relatively small amounts of blown fatty oils does not change the maximum elasticity modulus of this type of mixtures to any considerable extent.

Again, however, it should be realized that these auxiliaries increase the equiviscous temperature at the same time, so that, when comparing pure bitumens with such mixtures of equal creep tendency in the high temperature range of the application, the effect on the shear modulus may be reduced or reversed. No general conclusion in this respect can as yet be given; only in the case of polymerized fatty oils does the mixture undoubtedly compare favourably with a pure bitumen.

The breaking strength of these various mixtures has not been studied closely. It is known that the shatter test mentioned on p. 268 is considerably improved by the addition of small amounts (*e.g.* 5% by vol.) of non-fibrous fillers and by even smaller quantities of fibrous fillers.

Finally, the durability, as far as oxidation phenomena are concerned, is little affected by the addition of mineral fillers; this factor is governed by the influence of these fillers on the rate of diffusion of the oxygen. The influence of organic auxiliaries will depend on their oxidation stability, which may vary considerably and is generally lower than that of the bitumen.

§ 3. PROPERTIES OF THE SYSTEM ADHESIVE-ADHERENDS

(a) *Introductory*

In § 2 of this Chapter those properties of asphaltic bitumens or bituminous compounds have been discussed which are determinant factors in their use as an adhesive. Some general remarks, relating more particularly to properties of the adhesive-adherends system, may appropriately round off the discussion.

The uses of asphaltic bitumen as an adhesive can be divided into two classes, which may be described as the two- and the three-dimensional classes.

The first class comprises all cases where two parallel or almost parallel surfaces are bonded together by a thin layer of the adhesive ("laminating").

In the second class a large number of particles are united into a coherent mass by an irregularly formed three-dimensional honeycomb structure of the adhesive ("binding"). The filling of the voids between the aggregate particles may be complete or partial.

These two forms give rise to different stress distributions according to the theories expounded in Chapter V.

Examples of laminating are:

- (a) Manufacture of laminated paper (duplex or multiplex), in which two or more sheets of paper are cemented by a film of bitumen (e.g. 50 μ thick), to form a water-vapourtight packing material.
- (b) Manufacture of packing or building materials of analogous structure consisting of paper or board with metal foil, hessian with paper, boards, board with paper, etc.
- (c) Plywood.
- (d) Application of roofing or flooring felt on the spot.
- (e) Application of wooden blocks for parquet floors or of tiles.
- (f) Application of cork sheets, etc. for insulation purposes.

Some cases intermediate between laminating and binding are:

- (a) Surface treatment of roads.
- (b) Manufacture of coherent slabs of glass wool, etc.

Hot processes are generally used in most of these applications, except for the surface treatment of roads, where cold processes (solutions or emulsions) are usually preferred. Pure bitumens are mostly used; inorganic fillers are never added.

Examples of binding are:

- (a) Construction of bituminous roads, runways, floors, etc. of the hot or cold mix type.
- (b) Manufacture of bituminous tiles.
- (c) Manufacture of bitumen-bound cork sheets.
- (d) Manufacture of coal briquettes.

In the last three cases hot processes are generally used. In some of these applications the bitumen is mixed with inorganic fillers.

(b) *Processing and Adhesion*

It has been mentioned in § 2 b that for hot processing the corresponding temperatures are always within the limits of the thermostability of pure bitumens. In some cases, however, the temperature necessary in hot application may be too high for the thermostability of the adherends or of auxiliaries added to the bitumen, a fact which imposes careful forethought in the choice of the type of processing to be adopted.

The adhesion of the bitumen to the adherend is particularly sensitive to the conditions of processing. Satisfactory adhesion depends upon the bitumen's retaining the necessary low viscosity long enough to allow for the full completion of processing. Thus only can the bitumen adjust itself to the adherend, penetrate into pores or displace adsorbed layers, etc. There is, fortunately, no difficulty in establishing these necessary conditions

and good adhesion is seldom unattainable. It is only with highly polished surfaces, like chromium, that hard bitumens may present some difficulty.

There have been complaints of lack of adhesion between hard bitumen and pliant materials, such as rubber. In this case, however, adhesion fails when the bitumen begins to crack owing to excessively rapid deformation of the object, with the result that the bitumen layer peels off.

If hot bitumen is applied to a cold surface, it often sets too soon. As a precaution, therefore, the cold surface is first given a priming coat, consisting usually of a solution, but sometimes of an emulsion. The thickness of the priming coat normally amounts to 30–100 μ . Dip coatings are sometimes also applied; in this case the layer thickness amounts to about 250 μ . The bitumen of the priming coat should preferably be the same as that of the adhesive layer proper.

The surface of the adherend should be clean and dry; coating of wet surfaces often calls for special methods. Sometimes these methods may be quite simple; *e.g.*, moist cement can be primed with a solution of bitumen in an aromatic solvent like solvent naphtha. As a rule, however, a more complicated method has to be used (see § 2 (a)).

(c) *Mechanical Properties*

After the extensive discussion of the mechanical properties in § 2 (b), (c), (d) and (f), little need be added here.

The application of asphaltic bitumen, which is a thermoplastic material, will always be limited by creep or flow at the maximum temperature to which the cemented object is exposed and in a number of cases by brittleness at the minimum temperature.

The consistency at this maximum temperature will in most cases be just such as to meet the limit for creep, because for other reasons the material should not be harder than is strictly necessary. The mechanical conditions and demands (stress and time) will determine the minimum value of the permissible viscosity (consistency). This viscosity should therefore exist at the maximum temperature to which the cemented object is exposed. As has been explained in § 2 (b), the difference between the Ring and Ball softening point and the corresponding equiviscous temperature normally does not vary appreciably in a bitumen of the first group compared with one of the second or even, in some cases, with one of the third. Nevertheless appropriate performance tests should be carried out to serve as a guide for the right Ring and Ball softening point of the bitumen in this respect.

The brittleness of the bitumen may become a decisive factor at low

temperatures. In a number of cases bitumens with the highest attainable modulus of elasticity will still serve; in other cases, however, a lower modulus of elasticity will be necessary at the minimum temperature to which the cemented object is exposed. The stresses which may develop in the bitumen may be either of external mechanical origin or result from internal temperature contraction. In the first case the stresses may be calculated from a constructional analysis of the stressed object, in the second case from the figure for the thermal expansion coefficient of bitumen given on p. 258, and that of the adherend(s) (see Chapter 4).

The considerable differences which exist in elasticity modulus between the three groups of bitumen provide a standard by which a judicious choice of bitumen may be made for those applications in which brittleness at low temperatures is a point to be considered. The more exacting the demands, the more imperative will it be to use a bitumen of the third group; in exceptional cases the use of mixtures with sulphurized or oxidized fatty oils may be necessary.

(d) *Influence of Time on the Cemented Object*

The changes which pure asphaltic bitumen may undergo with time under the influence of water and of air have been discussed in § 2 (e) of this Chapter.

When bitumen is used as an adhesive, there are two other factors which sometimes come into play, the source of which is the porous structure of the adherend, or, on occasion, a faulty combination of primer and bitumen layer.

When bitumens of the first or second group are in contact with a porous material, they will gradually be absorbed into the capillaries. The rate at which this process of bleeding proceeds can be described approximately by the formula

$$\frac{h^2}{t} = \frac{2rS}{\eta} \quad (9)$$

where h = capillary rise (cm) in t sec.; r = radius of capillary (cm); S = adhesion tension (erg/sq.cm) and η = viscosity (poises).

This formula shows that the rate of this process is determined above all by the viscosity of the bitumen, there being no substantial differences in the adhesion tension. Therefore, equal rates of bleeding will be found at equal equiviscous temperatures. By reason of what was stated in § 2 (b), (iii), this means that this rate is chiefly determined by the difference between the Ring and Ball softening point and the temperature of exposure.

A calculation, in which a normal set of conditions is substituted in formula (9), shows that, as indeed practical experience bears out, this type of process is extremely slow and can only be observed in cases where thin layers of adherends are used.

When bitumens of the third group are in contact with porous materials, another process takes place. It was mentioned in § 1 (b) that absorption by porous materials may deprive bitumens of the third group of part of the oil phase of the gel structure. The rate at which this process takes place is determined by the capillary suction of the pore structure of the adherend, by the permeability of the gel structure and by the viscosity of the oil.

This phenomenon occurs with bitumens of a pronounced gel character. Its effects can often be mitigated by a judicious choice of the porous material (especially paper).

Finally, this same loss of oil phase by gel-type bitumens may result in the formation of a layer of low viscosity when these bitumens come into contact with bitumens of the first or second group, *e.g.* as an adhesive layer on a primer. In this case the oil of the former bitumen sometimes fluxes the latter, with, as a result, reduced coherence, or soiling of the object if the oily layer finds a loophole for escape. This is why the bitumen of the primer should be as similar as possible to that of the subsequent layer.

§ 4. CONCLUDING REMARKS

In the preceding sections the properties of asphaltic bitumen, in so far as they affect its use as an adhesive, have been reviewed.

We are led to conclude that different bitumens vary considerably in their rheological and elastic properties. As they vary far less in their other properties, the choice of the grade of bitumen considered most suitable for a given application is governed mainly by those mechanical properties.

As has been explained in § 3 (c), the allowable permanent deformation (creep) at the maximum temperature of the application determines the hardness, roughly expressed by the Ring and Ball softening point of the bitumen or the bituminous compound, whereas the requirements for resistance to fracture at low temperatures determine the type, as expressed by the first, second or third groups or, in other words, by the Ring and Ball softening point-penetration 25° C relation.

This statement is not only based on the fundamental knowledge of the rheological and elastic properties of bitumens as given in § 2 (b), (c) and (d), but is fully supported by experience.

This general rule is, however, not much more than qualitative, in that it relies mainly on a comparison between various types of bitumen. The reason for this is that the constructional analysis of most cementing processes is still in its initial stages; Chapter 4 gives calculations for a number of cases, but does not yet cover the whole field satisfactorily.

It will not be possible to formulate purely quantitative rules until the constructional analysis is complete.

Current general knowledge of the rheological and elastic properties of asphaltic bitumen seems to be sufficiently comprehensive to find a place in such analyses.

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CHAPTER 6

INORGANIC ADHESIVES AND CEMENTS

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The field of materials comprising inorganic cements is much wider than that of adhesives defined as a thin film between adherends. In general we here "divide between fluids which are applied as thin films to unite surfaces nearly in contact and the more viscous masses which, though they may be sticky and exert adhesive properties, are yet expected to occupy more space than adhesives proper"¹.

Uses in which material is present as a coating layer on a single adherend are not included although many such thick layers are made of cementitious compositions. Somewhat less characteristic of cements are the facts that they usually contain fillers which may be relatively large particles and that their set often depends on crystallization. The colloidal nature is not so preeminent a characteristic of the adhesive layer. Interfacial properties still control their use as surfaces must be wetted and a bond formed which is as strong or stronger than the weaker of the adherend or cement. At the same time there should be an adequate bond between the filler and the cement itself. In general cements find their greatest use in the building trades and the choice depends on the relative importance of cost, chemical resistance, and strength.

A. INORGANIC ADHESIVES: SODIUM SILICATE

§ 1. INTRODUCTION

While there are a few inorganic materials which form concentrated colloidal solutions, sodium silicate, because of its low cost, freedom from crystallization and wide range of properties is the only one in general use as an adhesive. Solutions of aluminum acetate² and sodium borates³ have adhesive properties but they are more expensive and in some cases tend to crystallize and become brittle.

VON FUCHS⁴ noted the adhesive qualities of the soluble silicates over

100 years ago and some minor commercial use was made at least as early as 1867^{5, 6} but it was not until about 1900 that use as a glue became of industrial importance⁷. At this time the replacement of starch by sodium silicate as the adhesive made possible the development of machinery for rapid production of corrugated and solid fiber paperboard. Next in importance is its use for sealing box flaps and in the production of paper, cans and tubes. Although soluble silicates are produced or used in nearly all parts of the world the adhesive use appears to be much more widely developed in the United States where the paper box is used so generally that it has become an economic necessity.

§ 2. STANDARD PROPERTIES

Soluble silicates comprise a continuous series of ratios of alkali oxide to silicon dioxide with any desired proportion of water. The cheapest soluble silicates are those of soda. Other alkali silicates are used only where their special properties make the difference in cost unimportant. Only certain representative ratios at stipulated concentrations are available commercially. Following the accepted nomenclature¹, a comma will be placed between the oxide symbols when the ratio only is indicated. Thus $\text{Na}_2\text{O}, \text{SiO}_2$ will not indicate a definite chemical compound. It is convenient, however, when using ratios, to employ the whole numbers associated with the inverse form $\text{SiO}_2 : \text{Na}_2\text{O}$. This form is used principally in the tables and figures and care must be taken to recognize the shift in emphasis. For adhesive uses, any commercial liquid grade of sufficient concentration can be used but the range is usually restricted between $\text{Na}_2\text{O}, 2\text{SiO}_2$ and $\text{Na}_2\text{O}, 4\text{SiO}_2$ and viscosities at the temperature of use varying from about 1 poise to 10 poises. Sodium silicate solutions approximating the analyses in Table 29 are normally available in most countries and special concentrations may be obtained when needed.

Sodium silicates with high viscosities are diluted as required. In general the ratios more alkaline than $\text{Na}_2\text{O}, 2\text{SiO}_2$, although quite viscous when concentrated, are not used as adhesives because of high alkalinity and instability. However, WARE⁸ maintains that for certain uses a mixture of $\text{Na}_2\text{O}, 3.2\text{SiO}_2$ with $\text{Na}_2\text{O}, 1.6\text{SiO}_2$ has advantages. He declares that the more alkaline part will react with added mineral powders while the more silicious will reduce the tendency to absorb water and allow drying at normal atmospheric temperatures.

At the concentrations used for adhesives, the pH is fairly constant for a given ratio because the sodium silicate solutions reach a maximum at less than 10% solids.

TABLE 29

PROPERTIES OF STANDARD COMMERCIAL SODIUM SILICATE ADHESIVES
(data determined at 20° C)

Silica: Alkali Ratio % by weight	%Na ₂ O	Bé°	Specific Gravity	T _w °	Viscosity Poises	pH
3.40	8.30	39.7	1.377	76	3.3	11.2
3.22	9.16	42.2	1.410	82	4.0	11.3
3.22	8.90	41.0	1.394	79	1.8	11.3
3.22	8.60	40.0	1.381	76	1.0	11.3
2.90	11.00	47.0	1.480	96	9.6	11.5
2.40	13.80	52.0	1.559	112	17.0	11.9
2.00	14.50	50.0	1.526	105	2.8	12.2
2.00	18.00	59.3	1.692	138	700	12.2
1.60	19.50	58.5	1.676	135	70	12.8

§ 3. CONSTITUTION

Sodium silicates in the ratio range of adhesive use are known to be colloidal systems. This has been shown by the extensive work of BURGESS ⁹, CANN ¹⁰, GANGULY ¹¹, HARMAN ¹², KOHLRAUSCH ¹³, STERICKER ¹⁴, SVEDBERG and co-workers ¹⁵.

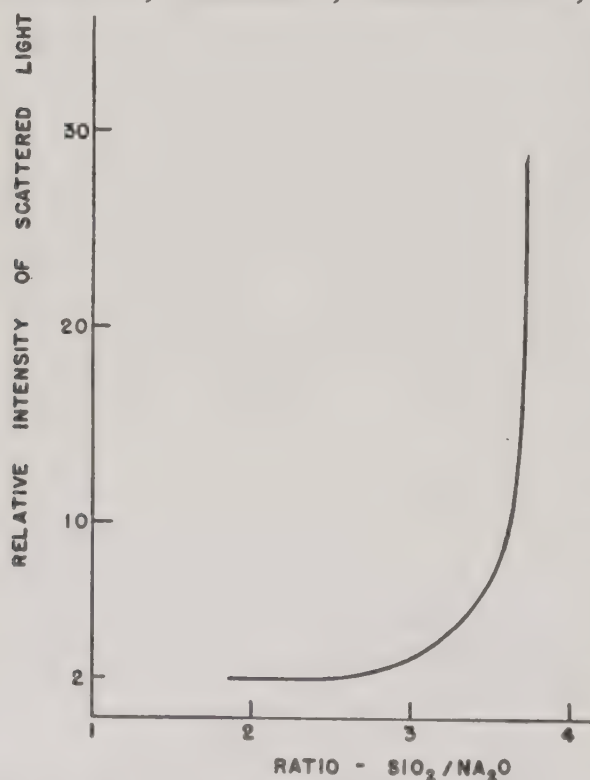


Fig. 91. Light scattered in an ultramicroscope from filtered solutions of 2M commercial sodium silicate adhesives (data by GANGULY).

GANGULY ¹¹ used an ultramicroscope to count the colloidal particles in somewhat diluted and filtered commercial silicates. He found that the number of particles increased very rapidly after a ratio of 3 SiO₂: 1Na₂O was reached. Experiments on the scattering of light, Fig. 91, osmotic pressure and relative diffusion rates also show the same rapid change at about this ratio. Conductivity experiments, estimation of the percentage hydrolysis, studies of the colligative properties such as the depression of the freezing point, activity coefficient and boiling point elevation all

show a break at a ratio of about $2\text{SiO}_2 : 1\text{Na}_2\text{O}$. At very low concentrations, this is not always noticeable. A strong continuous Raman spectrum is a property of viscous liquids. The strength decreases on dilution and increase in temperature. HIBBEN¹⁶ and GANGULY and CHAKRABARTY¹⁷ compared silicate solutions from 1 : 1 to a dialysed sol and concluded from the shift in sharpness of the band that the ionized particles had the same structure but a difference in aggregation.

Most of these studies have been fully reviewed by VAIL¹. They do not come into direct use in adhesive applications and are more closely allied to cohesion as discussed in Chapter 2. WILLS and SAMS have recently reviewed the colloidal character of sodium silicate adhesives¹⁸.

It is generally agreed that a commercial sodium silicate of adhesive grade is composed of colloidal electrolyte particles which are very little hydrolysed. These particles have a fairly high negative charge as shown by mobility studies of BILLITZER¹⁹, ZSIGMONDY²⁰ and HAZEL²¹. In fact they barely become electro-positive as the pH approaches zero. This character of a colloidal electrolyte explains much of the wide applicability of sodium silicates. They have not only the property of "deformability"²² as colloidal adhesives but they react metathetically with numerous surfaces to form a strong chemical bond. They may also react by condensation of the hydroxyl groups with similar groups on the adherend surfaces. WEYL²³ explains that the adhesive properties are caused by the reactivity of the Si-O-Na groups . . . "Colloidal silica does not have the sticking quality of a waterglass solution. It ages because its free reactive hydroxyl groups react with themselves, thus increasing the molecular weight of the substance and decreasing its chemical reactivity. One of the requirements of a good adhesive is the presence of reactive groups under conditions which prevent these groups from reacting with themselves. The hydroxyl groups of a silica gel have a tendency to split off H_2O and to form a permanent bond. This is less likely to happen if we use waterglass which does not have free Si-OH, but Si-O-Na groups. Nevertheless, these groups hydrolyze readily in contact with other materials, such as cellulose, and enter similar reactions at a glass surface."

§ 4. BOND STRENGTH

The final bond formed always contains some moisture unless heated to about 700°F (360°C). The presence of this water adds to the bond resilience which a dry glass does not possess. Fig. 92 although inexact shows that the residual water content of adhesive grades is significant even at

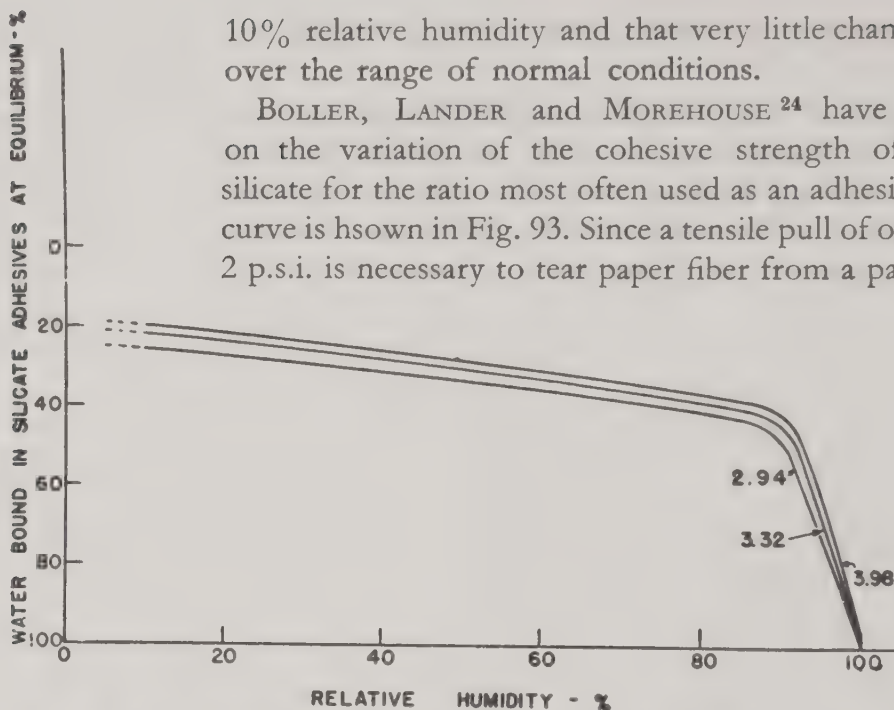
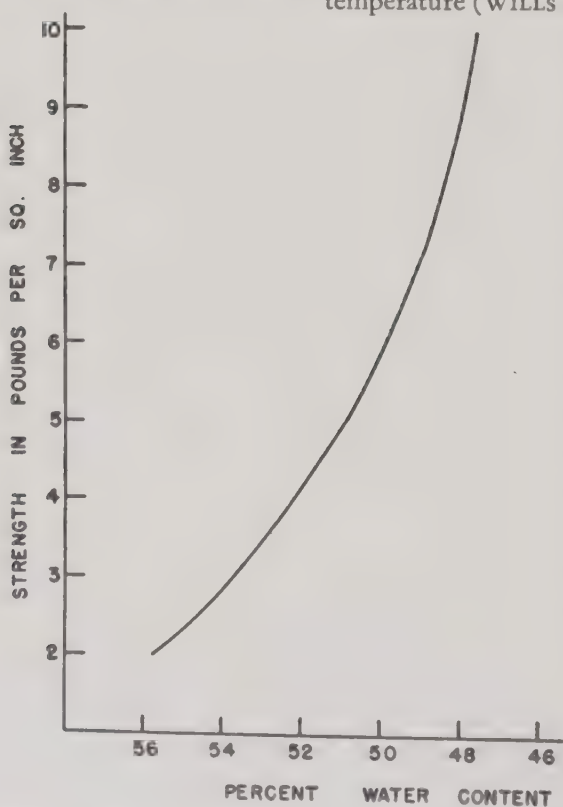


Fig. 92. The equilibrium moisture content of sodium silicate adhesives having $\text{SiO}_2:\text{Na}_2\text{O}$ ratios of 2.94, 3.32, 3.98 with varying relative humidity at room temperature (WILLS and SAMS).



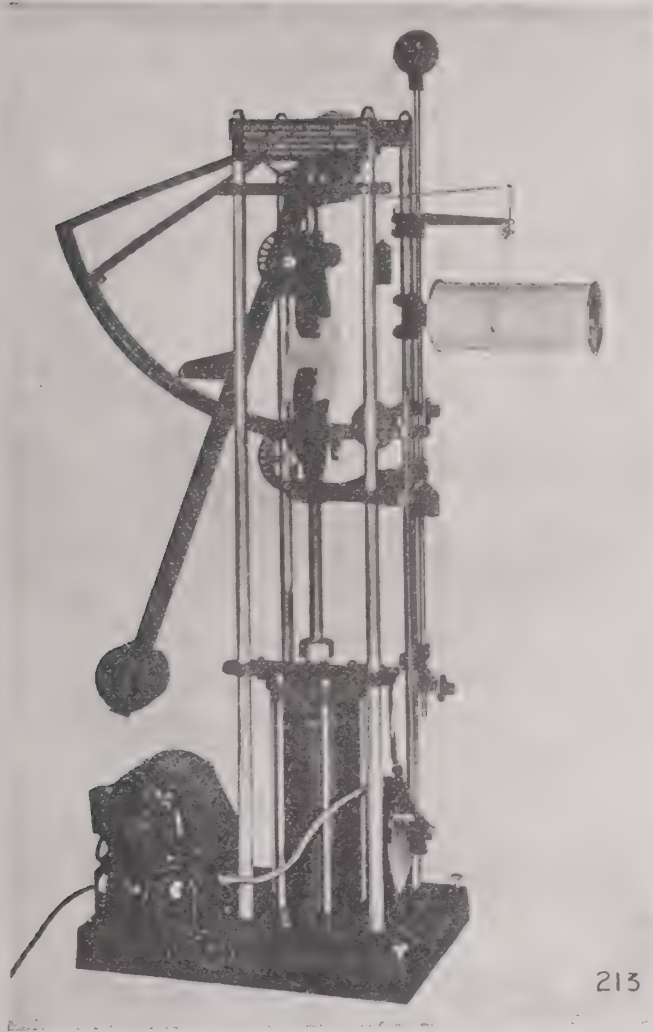
surface, it is evident that the adhesive soon makes a firm bond.

Because of this excess strength over that required for paper, MALCOLMSON²⁵ suggested the addition of NaCl as an extender. With such additives proper working characteristics may be maintained at greater dilution of the sodium silicate. GARDNER²⁶ suggested diluting the adhesive still further by the addition of fibrous talc which swells and helps to maintain the desired viscosity.

Fig. 93. Variation in tensile strength of a commercial $\text{Na}_2\text{O}, 3.3\text{SiO}_2$ solution with loss in water (BOLLER, LANDER and MOREHOUSE)

Dried bond strength has been tested under a number of conditions by McBAIN and his coworkers^{22, 27}. Thin films were prepared on thinly greased ferrotype plates or smooth celluloid sheets at about 55% relative humidity. Tensile strengths were measured with a Schopper dynamometer.

SiO ₂ : Na ₂ O Mole Ratio	%Na ₂ O	p.s.i.
3.0	9.1	500
3.0	9.1	600
2.9	11.7	300
2.45	13.8	150



Courtesy of Thwing-Albert Instrument Co.

Fig. 94. Electro-Hydraulic Tensile Strength Tester.

* Compare Chap. 4, section 2.

References p. 344

In a slightly different type of test, paper, was impregnated with the adhesive. A strip 0.007" thick showed a strength of 1,000 p.s.i. after correction for the strength of the paper itself.

These strengths are more than adequate for many materials but stronger bonds are found when the adhesive is backed with an adherend*. The addition of flint did not affect the strength appreciably. Bonds were obtained with all the materials tried except rubber and in some cases bond formation has been obtained even with this surface. Ceramic, crystal, metal and charcoal surfaces were tested. Table 30 indicates the range of the results they obtained.

Their results on walnut may be compared with data (Table 31) by BROWNE and BROUSE²⁸ who give several tables showing the strength of wood joints made with Na_2O , 3.25 SiO_2 at a density of 1.415. The free film strength at 30% R.H. and 27° C (80° F) was 1900 p.s.i. The adhesive was applied at room temperature without dilution and at 200 p.s.i. pressure.

TABLE 30

DATA ON STRENGTH OF SODIUM SILICATE BONDS BETWEEN MISCELLANEOUS ADHERENDS
AS DETERMINED BY MCBAIN AND CO-WORKERS

SiO ₂ /Na ₂ O	Test	Time of drying or setting (days)	Bond Strength in pounds per square inch										
			Nickel	Mild Steel	Cast Iron	Copper	Brass	Aluminum	Tin	Lead	Glass		Wood * Walnut
											single coating	double coating	
2.45	Tension	17	200	200	200	300	200	200	200	—	300	200	—
	Shear	17	200	200	200	200	200	200	—	—	—	—	400
2.9	Tension	17	500	500	500	600	500	400	500	—	1000	500	—
	Shear	17	400	500	400	500	400	400	400	—	—	—	500
3.0	Tension	26	1000	1200	1000	1100	1400	900	900	700	600	800	—
	Shear	26	600	800	600	1100	900	500	400	—	—	—	700
3.3	Tension	26	1300	1300	1100	1400	1500	700	1000	—	600	800	—
	Shear	26	800	900	800	1000	1200	700	700	—	—	—	400

* All walnut specimens were dried for 28 days.

TABLE 31

STRENGTHS OF Na_2O , 3.25 SiO_2 BONDS TO WOOD
AS DETERMINED BY BROWNE AND BROUSE

Compression Shear Tests (60 % R.H. and 80° F. (26.6° C))				
Test	Walnut Blocks		Maple Blocks	
	Ave. load at failure	Ave. wood failure	Ave. load at failure	Ave. wood failure
* RAE type	1550 p.s.i.	93%		
** FPL — old	1600	55%		
FPL — new	1900	40%	3000	68%

* Royal Aircraft Establishment. ** Forest Products Laboratory.

Side Grain Tension Tests (30% R.H. and 80° F (26.6° C))

	Ave. p.s.i.	Ave. wood failure
Gum	900	87
Walnut	950	72
Ash	1150	70
Beech	1100	88
Hickory	1100	66
Birch	1300	35
Persimmon	1450	69
Ave.	1150	70

§ 5. WORKING PROPERTIES

(a) *Viscosity*

The most significant working property of the soluble silicates is viscosity. Commercial solutions vary from viscosities comparable to sulfuric acid up to those approaching asphalt. If protected from loss of water and long exposure to the acidic gases of the atmosphere, the life is substantially limitless although after 2 or 3 years or storage at high temperatures some crystallization may occur at most ratios²⁹. While freezing ordinarily is not detrimental, solutions with ratios above about $2.4 \text{ SiO}_2 : 1 \text{ Na}_2\text{O}$, must be stirred thoroughly after thawing out.

According to the definitions by BINGHAM³⁰ all the silicate solutions encountered industrially are viscous liquids and not plastic solids, that is, they do not have a definite yield point.

There are numerous methods of measuring viscosity but only a few are applicable to the viscous solutions of sodium silicate which absorb or lose water depending on their ratio, concentration, temperature, and the humidity. Capillary tube methods are slow for such materials and the apparatus is difficult to clean and dry satisfactorily. Out-flow type viscometers such as the Saybolt or Engler should not be used because they allow too much exposure to the air and there is a tendency to become clogged by the formation of a film or scum on the surface of the silicate. The method which has been found most satisfactory for very viscous silicates above 10 poises is the one which depends on measuring the rate of fall of a steel ball. This method has been discussed by BACON³¹. In the method he used, a glass tube is centered over the top of the liquid with the bottom beneath the surface. Thus the steel ball which usually is $\frac{5}{16}$ " in diameter but varies with the viscosity, is released in a reproducible manner and its time of fall is measured over the central 16 centimeters of the tube.

He concludes "it appears . . . that with apparatus and methods of the refinement used the . . . method is capable of measuring absolute viscosity over the range 7.5 to 3060 poises to an accuracy $\pm 1\%$."

The Hoeppler rolling ball viscometer is relatively expensive but should be very satisfactory.

For adhesive grades of sodium silicate a falling ball usually passes too quickly for the time to be measured as accurately as desired. The method now most often used for control is that involving the rotation of a cylinder in the solution. The MacMichael, Brookfield, Doolittle, Brabender and Stormer viscometers are all of this type. Of these the Stormer has been found simple and convenient as well as rugged and is chosen by many laboratories for work with sodium silicates. In this type the speed of the rotation of the cylinder immersed in liquid and driven by a known weight is a measure of the viscosity of the liquid.

The viscometer itself must be calibrated against solutions of known viscosity. The U.S. National Bureau of Standards Circular 440 has suggested the use of sugar solutions at two different concentrations. A series of standard oils for which absolute and kinematic viscosity are known is also available³². Solutions of Sorbitol have been found very satisfactory as standard liquids³³. The viscosity of any of these may be determined directly by the use of the falling ball method and a standard calibration chart prepared to convert Stormer seconds to poises.

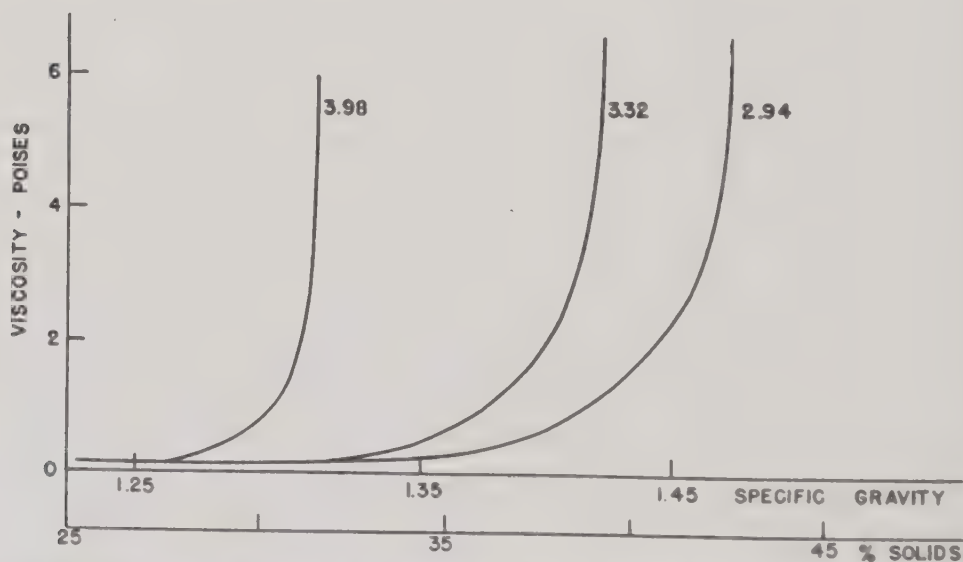


Fig. 95. Change of viscosity at 20° C of sodium silicate adhesives with concentration as determined by specific gravity and solids content. Adhesive ratios of SiO₂:Na₂O of 2.94, 3.32, 3.98 (VAIL and BAKER)

The Stormer seconds may also be converted to poises by measuring the bob weight required to produce 100 revolutions per minute and comparing this value with a standard curve set up from solutions of known viscosity.

For liquids of higher viscosity or which tend to show a yield point such as the clay-silicate adhesives it is sometimes advisable to add an extra weight, such as 100 grams, to the driving force of the Stormer viscometer in order to maintain sufficient speed of rotation.

The viscosity will vary with concentration of solids, ratio and temperature. VAIL¹ has shown the variation with Na_2O , SiO_2 , total solids, ratio and temperature. VAIL and BAKER³⁴ also show the variation of viscosity with concentration for solutions of the ordinary adhesive silicates (Fig. 95). ZAVJALOV³⁵ gives curves showing the change of viscosity with temperature and with dilution. (His results appear to be good except that 35.8° Bé at

3.5 ratio apparently should be about 36.8°).

BOLLER, LANDER and MOREHOUSE²⁴ also give the viscosity of 3.25 ratio silicate with total solids and temperature. Fig. 96, 97 and 98 shown here for the change of viscosity with alkali, temperature and ratio for a number of adhesive grades, are thought to be the most accurate now obtainable. At lower ratios the curves at constant solids content rise again as shown by VAIL¹.

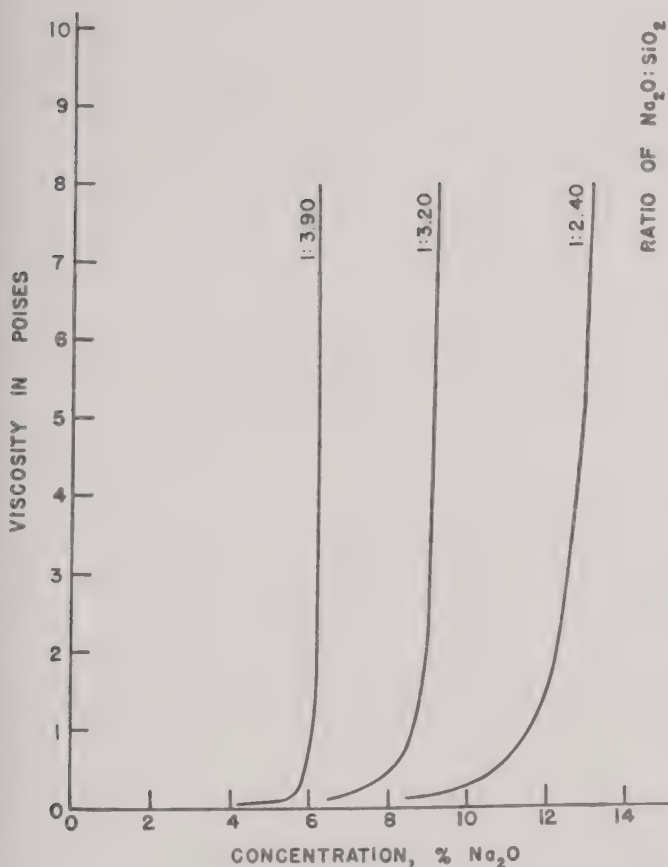


Fig. 96. Variation in viscosity at 20°C of sodium silicate adhesives with concentration as shown by alkali content.

(b) Tack

There has been no experimental data on tack added to the literature on sodium silicate adhesives since VAIL's

report¹ showing STERICKER's data on the relation of time and work to withdraw a suspended bob. This work, Table 32, shows definitely that adhesives do have tack aside from viscosity but it would be valuable to study them with a tackmeter such as that devised by GREEN³⁶.

The tendency in some technical circles is to define tack as the pull-resistance of a material adherend from two undeformed separating surfaces while the adhesive still exhibits viscous or plastic flow.

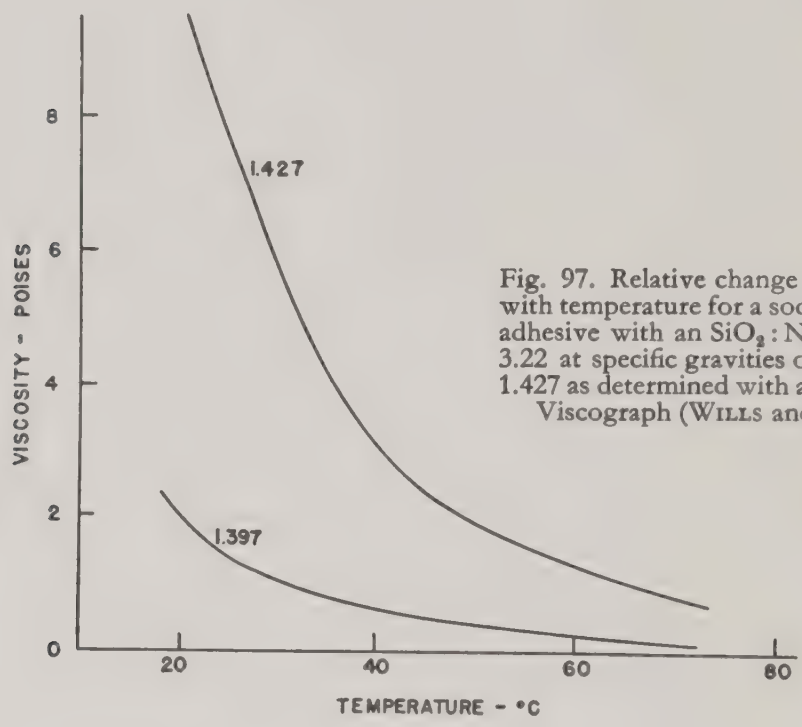


Fig. 97. Relative change in viscosity with temperature for a sodium silicate adhesive with an $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of 3.22 at specific gravities of 1.397 and 1.427 as determined with a Brabender Viscograph (WILLS and SAMs).

TABLE 32

COMPARISON OF TACKINESS OF OIL AND Na_2O , 2.1SiO_2 SOLUTIONS AT THE SAME VISCOSITY (from data by STERICKER, obtained at room temperature)

Material	Viscosity centipoises	Time in seconds with weight of			
		17.4 g	17.6 g	18.0 g	18.02 g
lubricating oil	124.5	too rapid to read			
Na_2O , 2.1 SiO_2 (diluted)	124.5				
Viscous oil	2704	21.5	2.1	4.5	2.6
Na_2O , 2.1 SiO_2 (diluted)	2549	44.4	11.3		

References p. 344

The general tendency among industrial users of soluble silicates is to compare both the pull-resistance and the length of the strings subsequent to initial separation.

No method adequately summarizes this phenomenon but the practical test employed is to rub the silicate between the thumb and the forefinger and then to note the ease of separation and the length of the strings *. These structures will be an inch or more long for a viscous Na_2O , 2SiO_2 solution and $\frac{1}{4}$ " or less for concentrated Na_2O , 3.9 SiO_2 solutions although the initial pull may be identical. Further the silicious silicate will dry out and lose its tack quickly while the more alkaline will maintain its tackiness for a long time. Since the pull-resistance is a function of time, surface area, and film

tackiness, each individual sets up his own standard of comparison.

No relationship has been shown between tackiness and the final strength or the setting time but tackiness does disappear as structure develops, (e.g. a gel). This may account for the fact that bond strengths have been found to decrease at ratios of SiO_2 to Na_2O above about 4.0.

Various efforts have been made to increase the tack of sodium silicate adhesives by the addition of other materials. While no data are available, the use of sugar, sodium phosphate and borax has been recommended from time to time ^{1, 37, 38, 39, 40, 41, 42}.

* Compare Chapter 3.

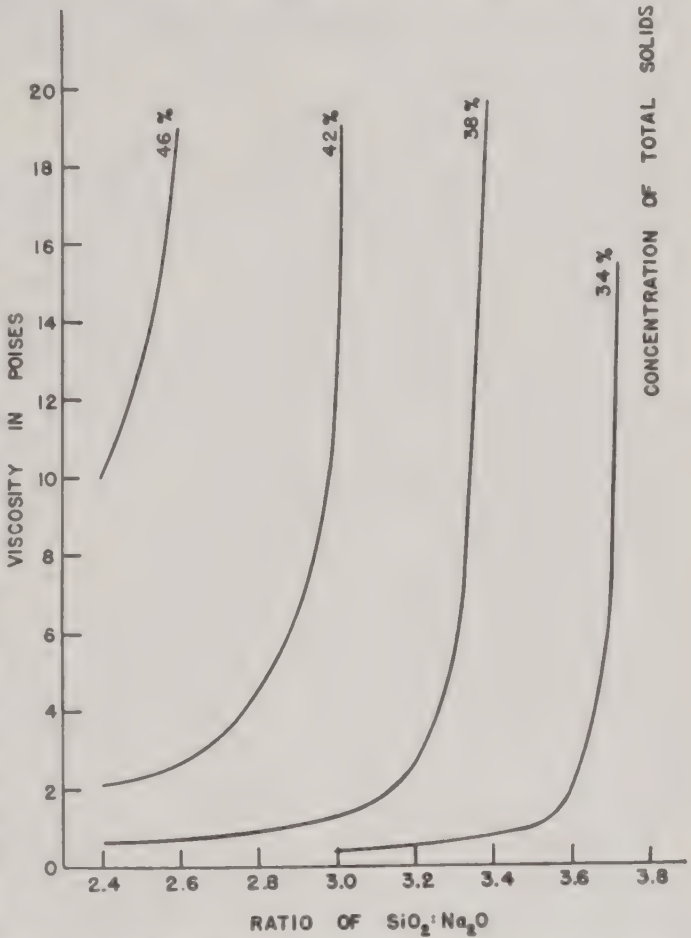


Fig. 98. The change in viscosity with $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of sodium silicate adhesives at constant total solids content of 34%, 38%, 42%, 46% at 20° C.

(c) *Wetting Properties*

There is considerable literature on the wetting properties of various sodium silicates. These properties depend on the material to be wetted as well as

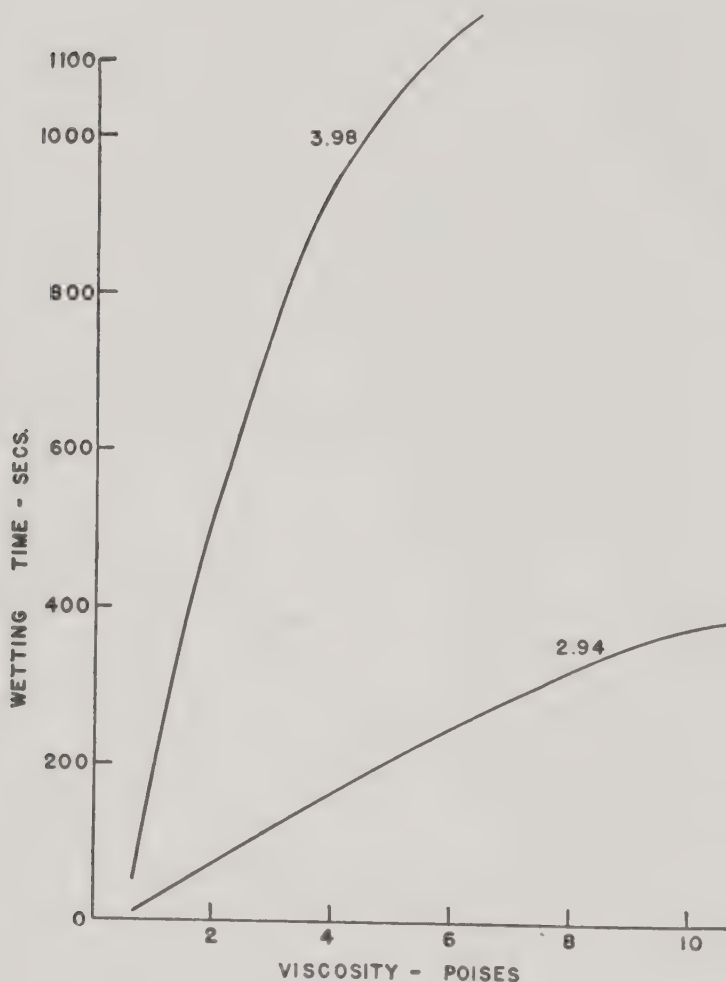


Fig. 99. The relative ease of wetting a standard filter paper by sodium silicate adhesives with $\text{SiO}_2:\text{Na}_2\text{O}$ ratios of 2.94 and 3.98 as the viscosity is varied at room temperature.

the alkalinity, viscosity and ratio of the silicate. Fig. 99 gives some idea of the variation in wetting time as affected by the viscosity and ratio of the silicate adhesive⁴³. The more alkaline ratio silicates wet rapidly whereas the more silicious and therefore more highly colloidal ones wet relatively slowly at the same viscosity. The wetting itself is proportional to the viscosity in both cases. These data were obtained by studying the rate at which #40 (110 mm) Whatman filter papers, dried at 105° and having approximately the same weight, fell away from a rod which forced them into the silicate of the given viscosity. In each case a weight of 0.3 grams was attached to the paper⁴⁰.

The surface tension of course is a guide to the wetting properties of a given liquid. LIDDIARD⁴⁴ compares the wetting power of diluted sodium silicates containing 1% Na_2O on glass surfaces. While these solutions were not comparable to adhesive concentrations they do show that the surface tension decreased with increasing colloidal content.

Alkali	Wetting Coefficient
1Na ₂ O, 3.3 SiO ₂	6.63
1Na ₂ O, 2 SiO ₂	3.83
1Na ₂ O, 1 SiO ₂	3.57
1Na ₂ O	2.52

McBAIN and SHARP⁴⁵ give the surface tensions in dynes/cm as the concentration of a sodium silicate solution (8.87% Na₂O, 28.37% SiO₂) in water is increased up to 20 g/100 cc, a one to five dilution well below the adhesive range. (Table 33).

TABLE 33

THE SURFACE TENSION OF A DILUTE SODIUM SILICATE SOLUTION
(8.87% Na₂O, 28.37% SiO₂) AS FOUND BY McBAIN AND SHARP

g SiO ₂ /100 cc	surface tension, dynes/cm	
	immediate	20 min aging
0	72.0	
0.145	71.5	71.7
0.290	71.2	71.6
0.580	71.2	71.6
0.870	71.3	71.6
1.160	71.8	
1.450	72.2	
2.175	72.3	
2.900	72.4	
4.350	72.7	
5.800	73.0	

McBAIN further reported that the minimum was not found with an Na₂O, 1.6 SiO₂ solution and that the surface tension increased twice as rapidly. This is undoubtedly an effect of the decreased colloidal properties.

Although sodium silicates are considered as wetting agents in themselves there is a long record of attempts to increase these characteristics by the addition of special agents. In 1919 CARLETON⁴⁶ added sulfonated vegetable oils to alkaline sodium silicates. Later LEMMERMAN *et al.*⁴⁷ suggested a number of wetting agents to be added to film forming compositions of sodium silicate. Most anionic and nonionic wetting agents are miscible. Those interested may also refer to BIDDLE⁴⁸ and WARE⁴⁹.

The addition of wetting agents generally tends to increase the viscosity slightly so that some water should be added if they are to be used for adhesive or coating applications. However, the use of these agents has

not been general because the initial wetting properties are already high and the addition of the wetting agent does not appear to increase the bond strength. Because of the increase in viscosity, the weight spread at given clearance is also increased and the total bond strength appears to be greater. However, when based on the weight of the adhesive present in the glue line the actual strength is slightly lower as shown by the following experiment with corrugated paperboard.

% Wetting Agent	Spread per 1000 sq. ft. (93 m ²)	Tensile Strength in lbs. per ft. of glue line
0.0	14	40.2
0.1	24	43.3
0.0	24	44.3

The properties of the adhesive used will depend a great deal upon the adherend. A very porous sheet would naturally absorb a thin adhesive film too rapidly whereas a dense or highly calendered sheet would not be sufficiently wetted by a viscous adhesive.

CAMPS-CAMPINS⁵⁰ related an equation for the penetration of size into paper capillaries to adhesive requirements. The factors to consider are pore size, wetting, liquid density and viscosity. The cubic feet of air per cubic foot of air free paper fiber calculated for different sheets is:

Jute	0.9 (25.5 l)	Chip liner or Groundwood	1.7 (48.1 l)
News Chip	1.1 (31.1 l)	Dry Finish	
Cylinder	1.2 (34 l)	Fourdrinier Kraft	2.0 (56.6 l)
Kraft		Water Finish	
		Fourdrinier Kraft	2.4 (68 l)

He concluded that dry finish Fourdrinier Kraft will take up adhesive more slowly than Jute since it has larger pores but the adhesive will penetrate further and more will be used. A film forming adhesive is needed. When the corrugated board industry shifted to more porous sheets, clay-silicate adhesive mixtures were provided to prevent staining through and to give more economical spreads.

A Kraft paper has a high content of natural wood size which resists wetting and there is an increasing tendency to use a highly rosin-sized board. Chip and Jute too, may be highly sized.

In order to assure good adhesion of paperboard liners, penetration should be of the order of 0.001 to 0.002". This penetration, as has been

indicated, can be regulated by control of viscosity and temperature. Penetration can also be increased by increasing the moisture content of the board or by slowing down the setting time²⁴. On the other hand, SCHUPP and BOLLER⁵¹ conclude that variation at viscosities ordinarily used is so slight that effects of penetration are not as important as is usually imagined.

(d) *Setting Characteristics*

Sodium silicate adhesives set by loss of moisture. They form supercooled liquids in the sense that glass is a supercooled liquid. The final product is hard and glassy and does not devitrify appreciably with age but may be attacked by CO_2 or other acidic gases from the atmosphere. The dried anhydrous residue has the high tensile strength and brittleness of ordinary glass. However, the presence of the small amount of water present at ordinary conditions (Fig. 92) increases resilience. The silicate adhesives lose water quite readily even at high humidity and then change very slowly as the relative humidity is reduced over a wide range. Even at rather low humidities some resilience may be maintained by the incorporation of such materials as sugar, sorbitol, glycerin, sodium alginate, and natural and synthetic rubber latex.

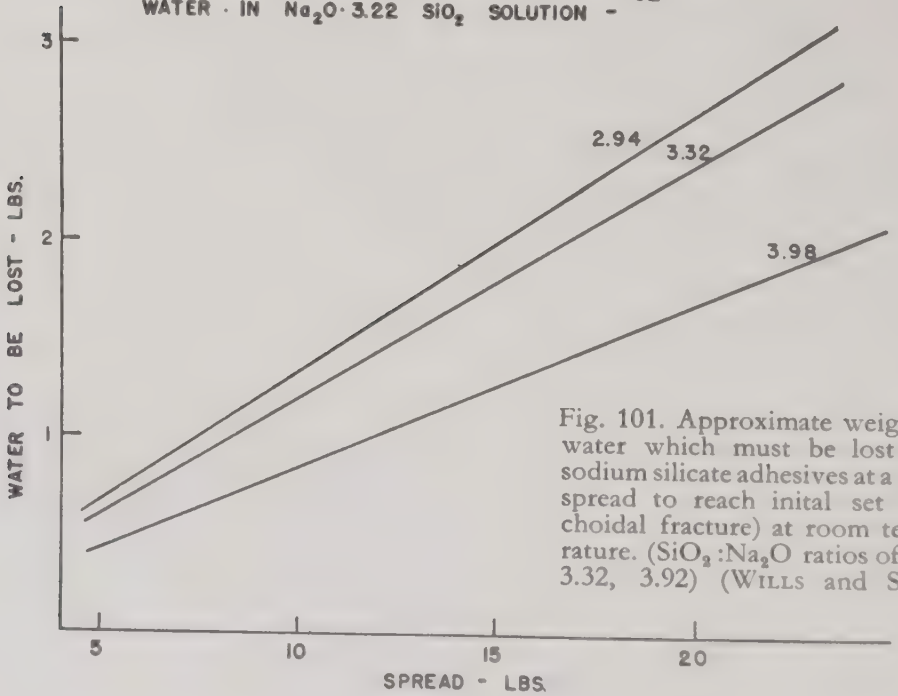
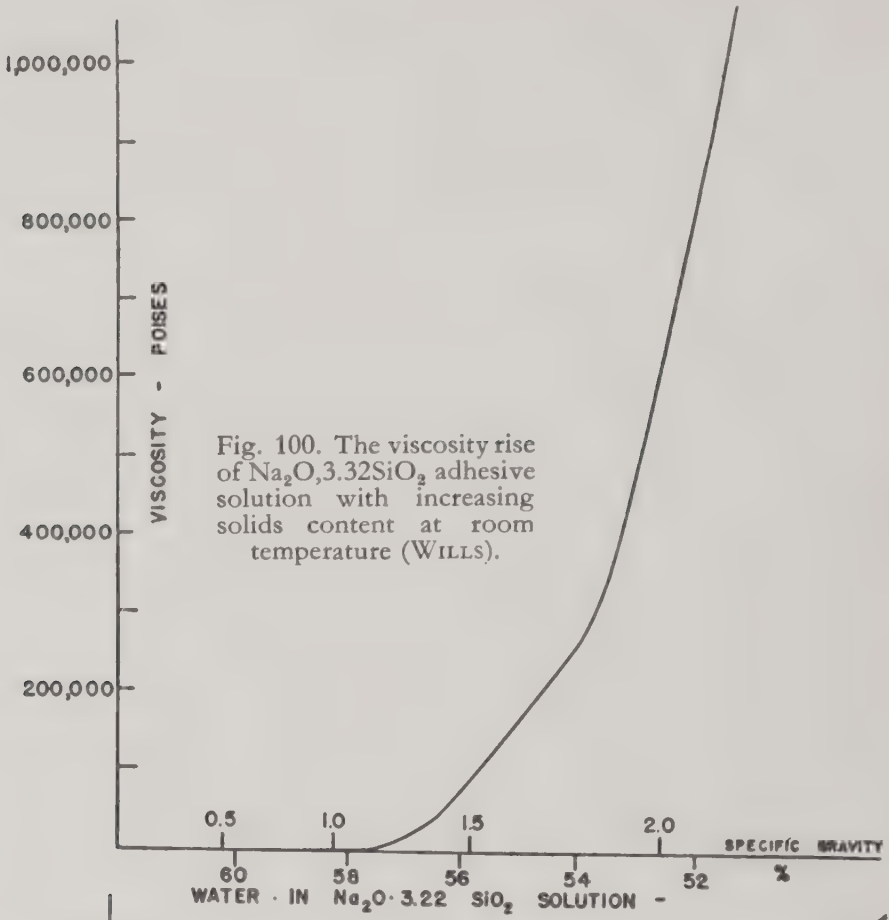
Silicates from $1\text{Na}_2\text{O}, 3.3\text{SiO}_2$ to $1\text{Na}_2\text{O}, 3.9\text{SiO}_2$ go through a stage of dehydration in which they may be bounced like rubber on a hard surface without cracking apart*.

Fig. 97 shows the rapid decrease in viscosity with increasing temperature. WOOD⁵² has suggested the use of this characteristic in increasing the rapidity of set but little commercial use has been made of the idea because of film formation in open pans. This is caused by rapid loss of water at higher temperatures and the low rate of diffusion into the surface from the mass of viscous adhesive¹⁰⁸.

Because of its colloidal character the silicate solution becomes plastic at relatively high moisture content. It will break with a conchoidal fracture but given time will coalesce. According to BICKERMAN⁵³, this defines the condition for set and ** STEFAN's equation ceases to apply. The actual conditions at initial set cannot be determined exactly as they will depend on the temperature of the bond. However, there does seem to be a definite range in which the rate of change of viscosity increase is a maximum and here conchoidal fracture appears. For a $1\text{Na}_2\text{O}, 3.3\text{SiO}_2$ solution this range appears to be at about 1.48 specific gravity (10.4% Na_2O) and approximately

* See Chap. 3, section on elastic, plastic behavior.

** See Chap. 4, section 11.



40,000 poises at room temperature. The rate of change of increase in viscosity ceases to rise as rapidly but viscosity itself continues to rise more rapidly indicating a shift toward a plastic and eventually a glass-like structure (Fig. 100).

Fig. 101 shows the water loss which is estimated as required to give an

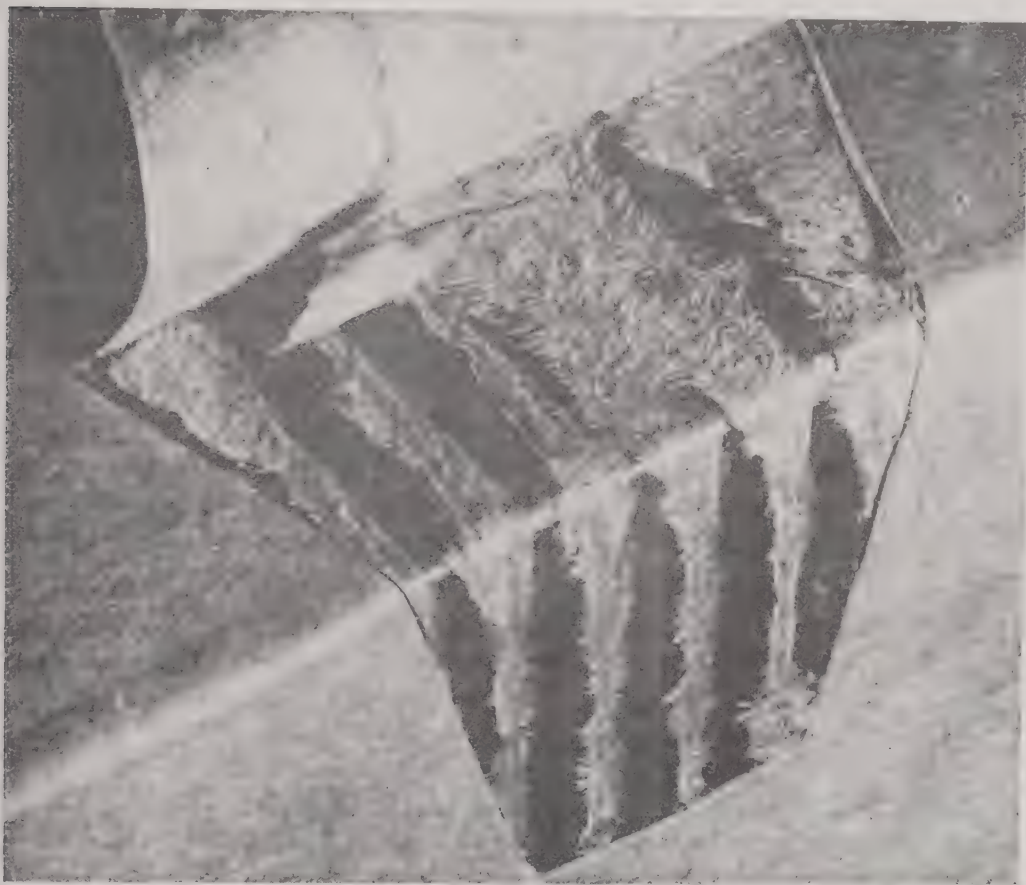


Fig. 102. The board torn over a crease shows a normal retention of the bond. The wide tear coverage is evidence of effective penetration and good shoulder formation.

initial set for adhesives of a series of ratios and of varying spread assuming that the curve (Fig. 100) for the $3.3 \text{ SiO}_2 : 1 \text{ Na}_2\text{O}$ ratio is representative. It is evident that the loss required will depend on the ratio as well as the original concentration.

Water loss required for set of sodium silicate is often confused with the loss required to reach equilibrium at room conditions. (Figs. 92 and 103). A comparison of Figs. 101 and 103 shows that not more than $\frac{1}{2}$ of the final loss is required for initial set. This is considerably different from

the action of the usual organic adhesives. They set in the presence of the original water content and the water is free to enter the laminated sheets.

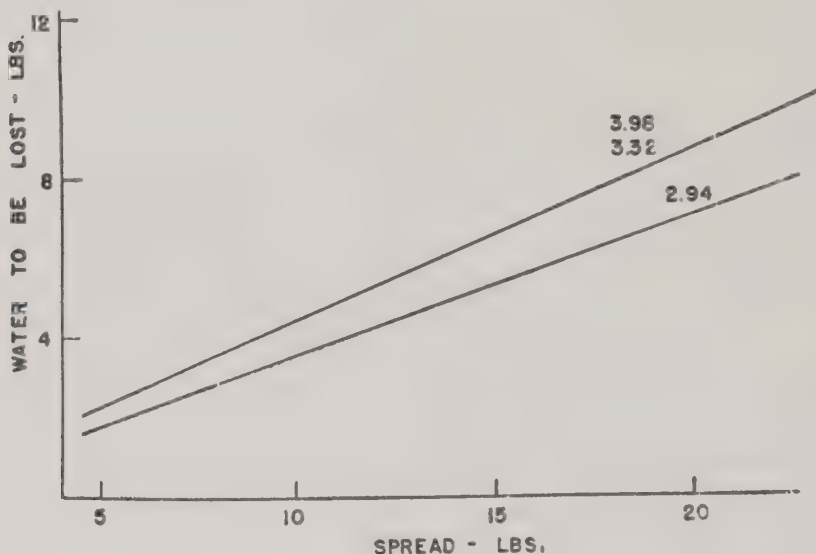


Fig. 103. Approximate weight of water which must be lost from sodium silicate adhesives at a given spread to reach equilibrium at room temperature and 50% relative humidity. (SiO_2 : Na_2O ratios 2.94, 3.32, 3.98) (WILLS).

(e) *Resistance to Pests*

Since sodium silicate adhesives are exclusively inorganic and alkaline, they are not subject to growth of molds and fungi. They actually resist the onslaught of ants or cellulose destroying insects¹ and rats and mice usually show little interest in boards made with these stiff hard films. It has been reported that the addition to sodium silicate of certain fungicides such as sodium pentachlorophenate will protect that portion of the corrugated paper not wetted by the silicate⁵⁴.

Silicious extenders to plywood glues prevented penetration beyond the first ply by limnoria, teredo, bankia. Pholads penetrate in greatly reduced numbers and are dwarfed⁵⁵.

§ 6. ANHYDROUS SODIUM SILICATE

While in general a silicate adhesive bond is somewhat hydrated there are cases in which the temperature is raised sufficiently to form anhydrous glass. For these cases it is worthwhile to include some references.

The thermal expansion of sodium silicate glasses from 0 to about 500° C is given by TURNER and WINKS⁵⁶. Table 34 shows the relation they found between thermal expansion and composition. The annealing temperature for such compositions is about 440° to 600° C.

TABLE 34

AVERAGE THERMAL EXPANSION FACTORS FOR 1% ADDITIONS OF Na₂O
FOR GLASSES CONTAINING 60 TO 91.6 PER CENT SiO₂
(assuming SiO₂ to be 0.05×10^{-7}) (TURNER and WINKS)

	0–130° C	130–250° C	250–350° C	350–Ct°
Linear Expansion factor $\times 10^7$	4.18	4.49	4.76	4.96
Cubical Expansion factor $\times 10^7$	12.54	13.47	14.28	14.88

TAYLOR and DEAR⁵⁷ found that YOUNG's modulus of elasticity was independent of temperature and determined the relations between viscosity and temperature.

HENDRICKS⁵⁸ discusses the structural elements of crystalline silicates based on a tetrahedral grouping of four oxygen ions around a central silicon ion. Closed groups, chain, sheet, and spacework patterns may result.

SUN⁵⁹ discusses glasses in general and records coordination numbers and metal-oxide bond strength for glass forming ions. A good glass former must have a low coordination number in order to keep the bond strength high and prevent orientation. Since the Na-O bond strength is low introduction of sodium loosens the structure of the glass. Presumably these factors have a relation to the adhesion to various surfaces. Adhesion to aluminum should be greater than adhesion to iron or bismuth but the bond strength of hydrogen and the heavy metals appears to range from about 40 to 70 kcal. with most about 50 kcal. Since adhesion to bismuth is much less than to iron the important factor is probably a failure in the metal-metal bond. This bond strength is lower for metals with higher conductivity and corresponding coordination numbers. The latter will vary according to the structure formed, *i.e.* crystal, glass or alloy.

The surface of the metal is also of importance. HILL and BURGER⁶⁰ found that glass would wet only an oxidized surface. Ni and C in metal surfaces also resist adhesion by glass. Ni alloys may be degassed only with difficulty and the bubbles they let loose weaken the adhesion*.

* Cf. Chap. 2 where the effect of polar substances on metal surfaces is discussed.

§ 7. REACTION OF SODIUM SILICATE WITH PAPER

The interreaction of paper fibers with sodium silicate adhesive deserves consideration. A paper sheet is a complex system since it includes cellulose, paper impurities such as lignin and filler materials such as rosin, alum, etc.

ROWLAND⁶¹ has reported the simpler system alkali-cellulose and shown that Na_2O is taken up very rapidly initially and approaches a maximum. MCLEAN and WOOTEN⁶² have shown that cationic exchange is reversible and varies with the grade of fiber. It seems to depend on the lignin, lignin cellulose and uronic acid, etc. impurities present. Kraft papers are much more active than most pure sheets such as linen. Discoloration can be prevented by the addition of oxidizing agents to the silicate⁶³.

The more complex and difficult system containing SiO_2 as ions and micelles has been touched upon. MCBAIN²⁷ found that the adhesive composition was changed very little except for the loss of water when applied to a paper surface. VAIL⁶⁴ described the action, applicable to other alkaline colloids, as a sort of dialysis which leaves most of the SiO_2 and Na_2O where it is laid down but some Na_2O is carried off into the fibers by the water. This is neutralized to an extent depending on the condition of the fibers and other materials present.*

WEYL²³ suggests that the silica reacts with the cellulose itself by hydrogen bonding and condensation.

A number of patents have been obtained covering the impregnation of pulp and paper to increase such properties as stiffness, toughness and wet strength. BRITT⁶⁵ and WEXLER⁶⁶ appear to be the first to give data showing a definite increase in wet strength through impregnation with either sodium silicate or a silica sol. The product of this absorption reaction is set by heating and the effect of as little as 0.1% SiO_2 is said to be noticeable. An increase in wet bursting strength from 0 for the untreated paper to 22 p.s.i. for the treated paper was recorded by WEXLER.

Special surface treatments have been used to improve the resistance of the bond to soaking in water. Cationic exchange may explain in part the specific effect of aluminum in the CARTER process⁶⁷ for water resistant board. The aluminum ion, the cheapest strongly charged ion, could replace hydrogen from cellulose in an aluminum chloride solution. The aluminum cellulose surface so formed could react with the sodium silicate to form an insoluble bond of aluminum silicate-cellulose having colloidal dimensions and therefore lacking the brittleness of crystallized silicates. The residual

* MERRIL and SPENCER⁶⁴ have found absorption of both Na_2O and SiO_2 by a variety of paper fibers.

chloride ions could neutralize the sodium ions and prevent desizing of the paper. Perhaps such ions as calcium and magnesium are not capable of reacting with the cellulose but only with impurities and leave an alkaline solution free to attack or desize the fibers.

Aluminum sulfate is not satisfactory unless chloride ion is also present. It has been suggested that free sulfuric acid parchments the paper surface and prevents reaction of the silicate with the cellulose.

§ 8. APPLICATIONS OF UNMODIFIED SODIUM SILICATE ADHESIVES

Sodium silicate solutions react with most metallic ions and often form cementitious substances which are useful in an adhesive sense. However, this review is confined by lack of space to those uses in which the sodium silicate or the sodium silicate mixture acts as an adhesive primarily by loss of moisture and is present in a thin film. It refers mainly to the literature subsequent to 1929. The early literature has been summarized by VAIL¹.

(a) Glass

Many are aware from personal experience that liquid grades of sodium silicate may form such a strong bond between glass surfaces or between glass and wood or stone shelves that the cohesive strength of the base is exceeded rather than that of the bond and chunks of the glass or other adherend may be torn out.

This bond is not resistant to water or to long exposure in saturated atmospheres when first formed but becomes more resistant by slow reaction with the glass or stone, etc. to form insoluble silica or silicates. An Na_2O , 2.9. SiO_2 solution has often been sold for the repair of ceramic ware. It has been observed for instance that such an adhesive sealed in a glass test tube will gel in about two years but it may be stored in an iron tube for as much as 30 years without an appreciable change in viscosity.

Sodium silicate solution are difficult to remove if allowed to dry on glass. The use of acetic acid followed with hot water and polishing with fine abrasives has been recommended and an application of H_2F_2 solution may be used if quickly rinsed off. It is much safer to use ammonium bi-fluoride⁶⁸ and better results are obtained. A 3% solution of H_2F_2 removed 1.5 mg per cm^2 of exposed glass surface per minute from eyeglass lenses while a 3% solution of NH_4HF_2 removed only 0.89 mg. H_2F_2 removed 39 g of film in 60 seconds and left the surface cloudy whereas NH_4HF_2 removed 64 g in 70 seconds without cloudiness. However, fogging was observed at 120 seconds of exposure.

The only recorded data on the tensile strength of bonds between glass

surfaces seem to be those reported in Table 30²⁷. These tests used commercial adhesives of varied ratio. The maximum strength appeared to be at $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of 2.9 to 3.0 but there is no way of knowing whether all of the data were obtained under optimum conditions for the individual ratios.

An interesting use is as the cement in the preparation of laminated glass sheets which resist dimming by the deposition of condensed water vapor⁶⁹.

Na_2O , 3.85 SiO_2 solutions extended with finely divided silica such as a gel or quartz meal have been found useful as a temporary cement for plate glass joints⁷⁰ and for glass to metal bonds⁷¹. The fine amorphous silica would tend to increase the ratio at ordinary temperatures while baking is required for the crystalline quartz which is insoluble in silicates more silicious than about Na_2O , 2.7 SiO_2 . Etching or frosting the surface is usually advantageous. WARE⁴⁹ made a permanently plastic adhesive for ceramic tile using a sodium silicate in the following composition.

36 gals (136 l) 60° Bé Na_2O , 2 SiO_2
160 lb (72.6 kg) asbestos fiber (stiffener)
128 lb (58.0 kg) asbestine (filler)
0.36 gals (1.36 l) sulfonated castor oil (surface active agent)

The adhesive is applied to the tile which is then pressed into place.

WALTERS⁷² found that the use of either spun glass or asbestos as a filler gave increased water resistance. This might be expected if the silica to alkali ratio was increased or some chemical reaction occurred when drying at a high temperature.

(b) *Metals*

The theory of the adhesion of sodium silicate glass to metal surfaces has been mentioned earlier. There seem to be no data on the wetting angles for the aqueous solutions on metals. The discussion on polar adhesives in Chap. 2 and on tensile strength of laminates in Chap. 4 should be reviewed.

One of the most general uses for sodium silicate as an adhesive for metals is in sticking aluminum foil to paper both for cigarette packages and for insulation board⁷³.

Difficulties which are sometimes encountered in forming a strong bond with aluminum may be traceable to dirty or passive surfaces. ROJAS⁷⁴ found that the metal could be cleaned with a detergent such as a dilute sodium silicate solution (5–10° Bé) or electrolytically, or by heating carefully to promote the formation of a clean active oxide surface. He then applied a layer of 40° Bé sodium silicate to the aluminum and sometimes

to the paper sheet and set the bond under gentle pressure and heat. He found that best results in the "cementing step are obtained with a relatively rough surface composed of innumerable pits and craters, and it appears that upon removal of gases, dirt and grease . . . the surface is so modified that union between the silicate glue and the metal occurs along the various ridges and crevices and a strong interlocking bond is attained thereat."

In some cases the viscosity is raised to as high as 41 poises by the addition of organic material such as carboxymethylcellulose, algin or sodium acetate ⁷⁵. These additives also usually increase flexibility in the bond. The adhesive is applied to the aluminum foil in streaks and must be chosen to avoid clogging the spray nozzles or attacking the foil under humid conditions, and to have adequate flexibility when forming the package.

In general a tacky viscous Na_2O , 2.9 SiO_2 solution is preferred. If high drying temperatures are used, powdered silicates and clay may be incorporated.

LACHMAN ⁷⁶ used rosin-soluble silicate compositions as adhesives for laminating aluminum sheets.

Similar adhesives have been used to apply sheets of copper to walls and ceilings and for laminating plywood to sheet steel or lead for X-ray rooms.

To overcome the difficult problem of applying polyvinyl halide to metal BENSON ⁷⁷ first coated the metal with soluble silicate and then pressed on a layer of fabric. The composition was then coated with the polyvinyl halide.

Metal clad fire doors are bound to an asbestos core with a sodium silicate such as Na_2O , 3.3 SiO_2 specific gravity 42° Bé ⁷⁸. Stainless steel would be preferred where high humidities are encountered. On ordinary iron and steel, galvanized zinc and red lead coatings instead of giving protection react with and thus reduce the protective action of the sodium silicate.

Another interesting use as an adhesive is that described by VAIL ¹. Minute watch screws are positioned in a polishing head by drawing them into holes with a partial vacuum and then coating the head with a viscous silicate. This holds the screws in proper position until they can be polished.

Rock bits are hardened by facing the teeth with particles of tungsten carbide. The tooth faces are coated with sodium silicate as an adhesive for the tungsten carbide particles which are sprinkled over the surface. The particles are thus held in place while they are fused onto the metal base with heat from an oxyacetylene flame ⁷⁹.

This use is somewhat similar to the process described by MITCHELL ⁸⁰ for forming a chromium alloy surface on a casting. Sodium silicate was used to bind chromium metal granules to the inner surfaces of the mold before pouring.

(c) *Wood*

It has been shown that sodium silicate when properly used may furnish as high strength bonds for wood as does animal glue. The silicate is cheap and easy to apply. The major drawbacks to a larger use are the tendency to dissolve when wet and a lack of flexibility.

Plywood for temporary service, such as box shooks made from gum and poplar wood or for boxes used in the tea and rubber trade may be made with sodium silicate ⁸¹.



Fig. 104. The manufacture of plywood shooks for shipping cases.

BROWNE and BROUSE ²⁸ have indicated that a strength of the "same magnitude as animal glue" may be obtained if the sodium silicate is used at a viscosity high enough to avoid running into the interstices of the wood. In their work they used a pressure of about 200 p.s.i. The low values found by MCBAIN *et al.* ²⁷ were traced to starved joints which resulted from too great dilution of the silicate adhesive. Penetration depends on the size and numbers of the pores in the wood, pressure exerted in assembling and the fluidity of the adhesive.

VAIL ¹ describes the equipment and technique which is often used in the cold process. In brief, a two roll glue spreader is used to carry the adhesive from the pan onto opposite sides of the center sheet of a 3 ply veneer. 85–90 pounds per 1000 sq. ft. (0,041 kg–0,044 kg/100 cm²) is applied to

each side. The adhesive is usually Na_2O , 3.22SiO_2 , 41° Bé solution but contrary to a general impression a higher concentration may allow a longer working period because the tack will hold the plies in contact. The center sheet is layed crosswise of an outer sheet and again two more sheets placed on top. The process is continued until about 30 sheets of plywood have been piled up. They are then put into a press and allowed to stand, preferably overnight. Pressure applied may be from 60 to 200 p.s.i., and piles should be put into a press within 20 minutes after the first center is layed. No attention need be paid to ventilation as the loss of moisture into the wood is sufficient to set the bond and to allow cutting.

The hot press method uses either dry or wet veneer. The plates are heated and only one or at most a very few panels are inserted between the hot plates at one time.

A corrugated plywood which is stiff when the corrugation is parallel to the grain can be formed by laminating a paper sheet to a thin wood strip using a mixture of sodium and potassium silicate with glucose, calcium carbonate and a sulfonated fatty oil. This wet laminate is fluted on a hot roller and glued to flat wooden webs. Glue on the tips is set on a hot plate as in the manufacture of corrugated paperboard ⁸².

CARTER made a study of the effect of age on the bond strength with maple blocks ¹. He found a rapid drop in strength from about 900 pounds down to about 350 pounds in the first eight months. Thereafter the strength was constant for at least 4 years. If the initial drop in strength is due to reaction with absorbed carbon dioxide and a gradual granulation of the colloidal film as is suggested, it is difficult to understand why the bond did not continue to deteriorate. Exposure to water will also cause a rapid reduction in strength. CARTER ⁸³ has indicated means for increasing the resistance to water and high vapor pressure and also preventing staining of the wood by the alkaline sodium silicate solution. Staining may be avoided by first coating the surface with various reactive salts such as iron chloride, barium chloride, calcium chloride or preferably magnesium chloride. Coating with ammonia or ammonium salts is also practical. In a later patent ⁶⁷ he discovered that aluminum chloride not only prevented staining but also provided a highly water resistant bond.

There are a number of protein silicate mixtures described in section 16 c of this chapter which also have high resistance to water.

Dovetailed wooden boxes are glued by first dipping the ends in silicate of soda and then setting in place. Trunks and trunk trays are often made by gluing a layer of vulcanized fiber * to the base wood. In some cases an

* Vulcanized fiber is paper treated with ZnCl_2 and steam under pressure.

intermediate paper ply is used and in others the adhesive film is allowed to dry tack free and then combined with the vulcanized fiber in a hot press. The fiber is then varnished to increase its resistance to moisture.

Various insulation masses are used in which the sodium silicate acts both as binder for the fibrous fillers and as adhesive to the base ⁸⁴.

(d) *Paper*

The major volume of silicate adhesives is used on paper. The specific effects are covered in Sections 7 and 9 but one interesting use of a paper or treated paper adherend is in forming abrasive coated fabrics (sand paper). A layer of adhesive is applied to the surface and granules of quartz or other abrasive are pressed into the surface before drying ^{85, 86}. Where calcium carbonate is used to increase water resistance, a $1\text{Na}_2\text{O}, 2.0\text{SiO}_2$ silicate of soda is preferred, but the more siliceous ratios are more resistant to aging and protective coatings may be applied ⁸⁷.

RICHMOND ⁸⁸ suggested a water resistant stable composition of

5 lb. (2.268 kg) asbestos cement
0.5 lb. (0.2268 kg) ZnO
1 gal. (3.785 l) sodium silicate
4 oz. (0.113 kg) glycerin
0.25 lb. (0.1134 kg) rosin

and ROBIE ⁸⁹ advanced a mixture of soluble silicate and aldehyde urea composition hardenable by heat.

Where "blooming" (formation of a white film of crystallized sodium salt) is objectionable, potassium silicates are recommended.

§ 9. CORRUGATED PAPERBOARD

(a) *History*

The history of corrugated board begins with the patent LONG ⁹⁰ obtained for the production of a single face corrugated type of board. The patent by THOMPSON ⁹¹ is also important because it is the first to show the application of the adhesive to the flute tips only. Through nearly all of this interesting and revolutionary development described by BETTENDORF ⁷ sodium silicate has been the principal adhesive.

It has been and still is the most efficient and economical adhesive used in making corrugated boxes. It can be used as received in large tank cars or drums. The cost of mixing and the possibilities of human error involved

in the preparation of adhesives requiring mixing in the box plant are eliminated. Where freight cost makes the shipment of the liquid grades uneconomical solid grades may be shipped and readily dissolved in the plant by the use of pressure dissolvers.

By far the largest industrial use of sodium silicate as an adhesive is in the manufacture of corrugated paper board boxes for the manufacture of shipping containers. This production has grown figuratively by leaps and bounds in the last half century of industrial development in the United States as the following statistics indicate ^{92, 93 *}.

	Total Paperboard (tons of 2,000 lbs.)	Portion as Container board
1899	about 400,000	
1929	about 4,250,000	2,000,000
1945	9,796,995	5,527,676
1946	10,525,813	5,835,068

The average rate of production of corrugated paperboard has increased rapidly from about 10 feet per minute in 1895 until today there are records of production at the rate of 550 fpm. (see Table 39).

(b) *Paper, Specifications and Tests*

Container board which is the paper board made for the corrugated and solid fiber shipping container industry may be divided into the corrugating medium, liner board and chip board ⁹⁴.

Corrugating materials are usually 0.009" thick (9 pt.). The principal raw materials in the United States are now straw and kraft. Chestnut is passing and bogus are now more often encountered.

Liner boards are usually 0.010 to 0.030" thick, *i.e.* 10 pt. to 30 pt. Fourdrinier kraft and jute are most often used but all-sulfate and filled sulfate kraft are widely used also.

Fiberboard boxes are usually made to meet definite specifications such as those of the British Standards Institution, London and in the United States the Consolidated Freight Classification Rule 41 ⁹⁵.

QUINN ⁹⁶ in an article, *Basing of Container Standards Upon Performance* outlines the trend to performance testing of paperboard and paperboard boxes. He lists as the most necessary tests tear strength, crush resistance, burst or puncture, and the drop test. Later he has advocated the use of

* Statistics and descriptive material apply primarily to U.S.A. and may not parallel European practice. The equipment is largely the same but data are not as readily available.

the drop test, the inclined plane test or the revolving drum depending on the contents of the box and the usage it is likely to endure.

Standard methods of testing are being continually revised and new methods developed. Those tests already standardized may be found in

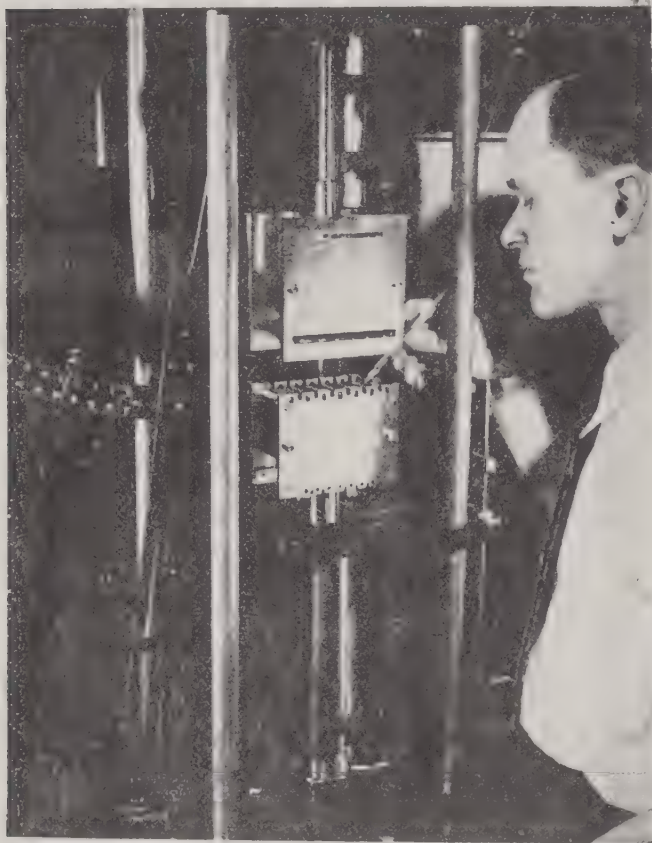


Fig. 105. Equipment for testing bond strength of corrugated paperboard used in instrument shown in Fig. 94.

the publications of the ASTM ⁹⁷, B.S.I. ⁹⁵ etc. Other methods though often used are less well standardized ⁹⁸.

The MULLEN or CADDY burst test has been the standard for many years and so much control data have been obtained that it is difficult to dislodge this test in spite of the lack of precision in results obtained with it. The Institute of Paper Chemistry ⁹⁹, ¹⁰⁰ recently has made a detailed study of the method and found a number of important variables which are not usually controlled.

The BEACH puncture tester ¹⁰¹ has been accepted by an increasing number of testing laboratories. In this test instead of expanding

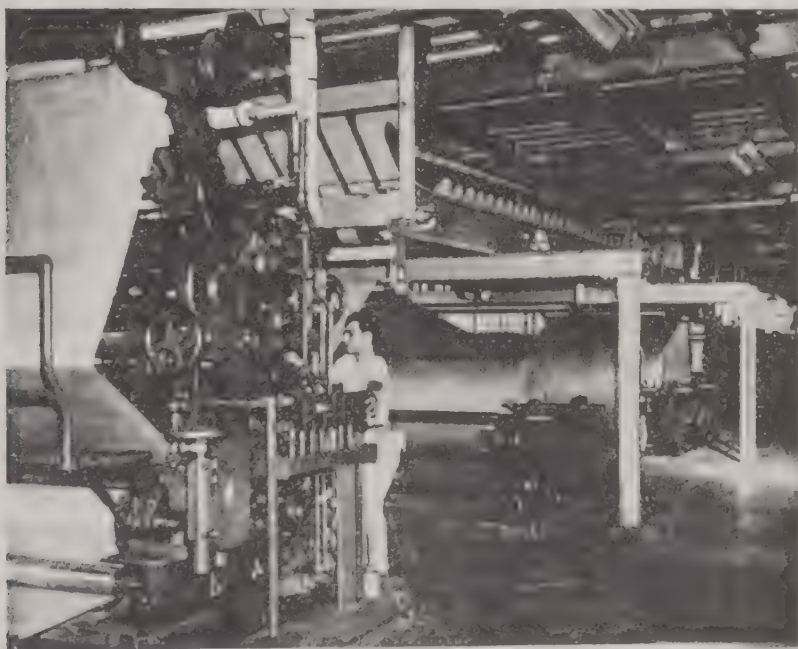
a rubber disc as in the burst test, a spear-head simulating a box corner is driven through the board. There are indications that this test may correlate with performance data.

LITTLE ¹⁰² has accumulated data "which indicates that the top to bottom compression resistance of box shapes may be predicted with reasonable accuracy from two separate properties of the corrugated board: (1) the compression strength when bending is reduced to a minimum, and (2), the stiffness factor (EI) expressed as the product of the modulus of elasticity and the moment of inertia." MCCREADY ¹⁰³, CARLSON ¹⁰⁴ and QUINN ¹⁰⁵ have also studied such relationships.

A number of laboratories including the Shipping Container Institute and the Institute of Paper Chemistry are carrying out detailed programs to determine which performance tests are most useful in judging the value of a fiber shipping container.

(c) Manufacture of Corrugated Board

The literature describing production methods has increased greatly both in quantity and quality in the last 20 years. The essential methods are still



Courtesy Samuel M. Langston Co.)

Fig. 106. Double deck 85 in. corrugating and single face unit with double-backer in far background

the same as those described by VAIL¹. However, mechanical improvements in the machines and steam systems have allowed machine speeds of over 500 fpm and the introduction of preheating rolls, glue circulating systems, corrugator roll lubricants, etc. have helped the paper and glues to keep up with the increased speeds.

Sodium silicates are particularly adapted to high speed practice as they wet rapidly, set quickly with low moisture loss, and require comparatively little heat input. These advantages are found most effectively in the mixtures with clay. High speed operation has also introduced the need for careful technical service by the adhesive manufacturers and a great advance in the technique of operation^{106, 107}

A brief description of the use of an ordinary silicate adhesive will explain the process of manufacture. A common machine such as shown in Fig. 106 first forms flutes or waves in the 9 pt. straw paper by steaming the whole surface with a contact type shower and passing the paper thus softened over a fluted brass steam-heated roll. Silicate is applied immediately to the flute tips by a glue roll and a sheet of liner is pressed tightly in place within a fraction of a second. The pressure in the pressure type machine is of the order of 150 p.s.i. The bond forms nearly instantaneously and this single face sheet is passed over a drying "bridge" to the "double backer" glue station. The glue roll clearances are set carefully to give an adhesive spread of about 7 to 10 lbs. per 1000 sq. ft. At the "Double facer" glue station, the adhesive is applied to the opposite flute tip and pressed onto the second liner with a continuous belt weighted by iron rolls to give a pressure about $\frac{1}{10}$ of that at the single face. The adhesive spread is usually a little higher to take care of irregularities in the sheet and about 10–12 pounds per 1000 sq. ft. is recommended.



(Courtesy Samuel M. Langston Co.)

Fig. 107. Cut-off section of 85 in. double face corrugated board machine showing hot plate and cooling section in background.

The silicate spread required will depend on the related factors of adhesive viscosity, composition, paper structure and moisture content, and machine conditions. The proper adjustment of each of these for highest efficiency is a matter of engineering ability and experience in production. Generally the total spread will be 16–24 pounds per M (1000 sq. ft.) (78–117 kg per 1000 sq. meters) for A flute and 15–30% higher for B flute double face board. A heavy board requires somewhat more adhesive. A 20 or 25%

increase in spread over the minimum required by the machine, and close supervision will more than repay its cost by a significant improvement in board strength.

The bond is set by passing it over steam heated plates – the “hot plate section”. This is necessary because of the higher spread and lower pressure at the double facer. A cooling or curing section serves to confine the moisture previously transferred from the adhesive by absorption into the liner and medium. This confined moisture reaches equilibrium throughout the three sheets of paper and therefore tends to stabilize dimensional changes which frequently cause warp and other handling problems. The continuous sheet then reaches the “cut-off” where it is chopped into “box blanks” of convenient size. These are stacked to cure and overcome any tendency to warp.

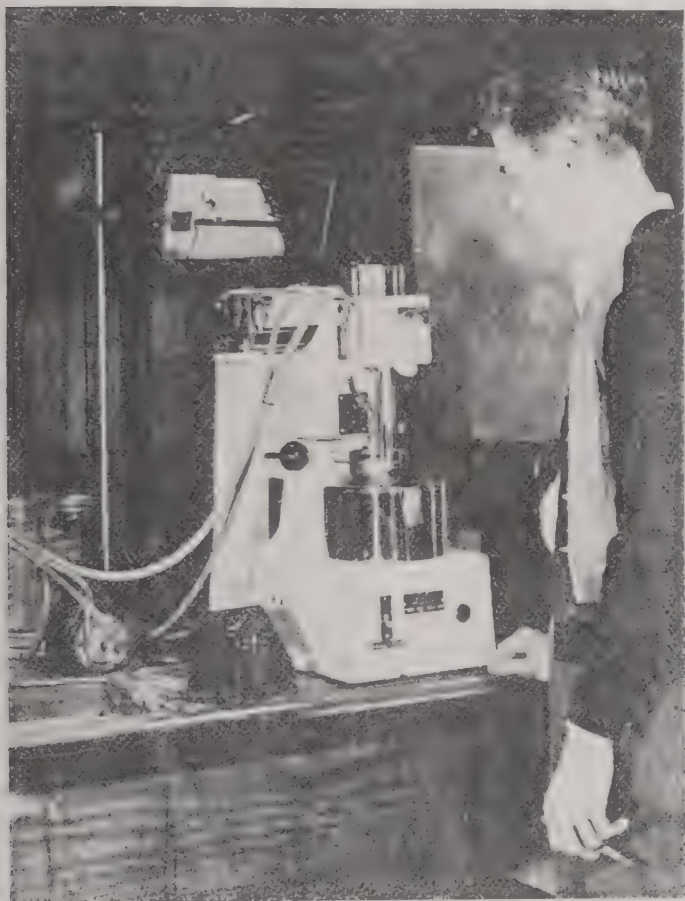


Fig. 108. Laboratory control and study of hot sodium silicate-clay adhesives is carried out with a recording Viscograph.

(d) *The Silicate Adhesives commonly used*

The tendency today is toward adhesives which will wet rapidly and yet set quickly with a minimum transfer of moisture to the paper. This has meant a tendency to use more silicious solutions such as Na_2O , 3.4 SiO_2 and higher, more concentrated liquid phases, starch and clay content, and hot adhesives in the glue pan. By a judicious use of these factors, along with

preheated board, an almost instantaneous "flash" set can be procured which will give a satisfactory bond without increasing the length of the hot plate and cooling sections. In fact these sections may be reduced in length if desired¹⁰⁸.

In general the advantages of sodium silicate adhesives for corrugated paperboard production are claimed to be the fast set because of low heat and moisture loss required for initial set, a lower spread, less warp and less washboarding, and a firmer and drier board at the take-off allowing more rapid use in subsequent operations.

The bulk of silicate-laminated container board is produced using the straight sodium silicate which has been designed empirically to give acceptable performance on both the single facer and the double backer. This depends primarily on maintaining the proper viscosity, and the liquid grades of silicate are controlled very carefully within the specified viscosity limitation by the manufacturers. The choice between 31° Bé Na_2O , 3.3 SiO_2 solution and 39.7° Bé Na_2O , 3.5 SiO_2 solution appears to depend largely on individual preferences and manufacturing conditions. Both silicate solutions are controlled in viscosity to permit the lowest possible penetration into the fibers before sufficient heat can be transferred into the liner. Build up of the adhesive on the fingers or rolls usually sets a maximum operating speed of about 225 fpm for pressure type single facers. On non-pressure single facers and double backers the maximum speed is set by the approximate 15 seconds required for initial set and allows speeds up to about 300 fpm to 400 fpm depending on the length of the hot plate and cooling section.

These straight silicate adhesives prove most satisfactory at moderate speed and with uniform paper. When heavy liners are used such as 30 or 23 pt., or double wall combinations are required, speed must be reduced greatly to provide the necessary heat transfer and proper equilibrium. When damp board or board which is more absorbant than usual is used penetration may be extensive and require a flooding of the glue line which results in a brittle board. Such board is also more liable to staining.

The single facer can use a thinner silicate than the double facer. This practice allows the transfer and corrugating rolls to be set closer. It also reduces build-up and wear on the fingers, provides better coverage of the finger gaps and less skin formation in the pan. A dual adhesive system therefore improves the uniformity of the glue pattern and allows higher speeds. The ordinary Na_2O , 3.2 SiO_2 solution is diluted to 37° or 40° Bé for use on the single facer. A controlled jet of water automatically provides the proper dilution. The heavier, more viscous grade of silicate used on

the double backer provides reduced spread and decreased penetration. The faster set, particularly on heavier board, improved adhesion and lower heat requirement results in colder, flatter and smoother board at the take-off.

Addition of clay to a diluted sodium silicate can produce an adhesive of slightly reduced moisture content and with more positive control of penetration and set. It can be used on either or both the single facer or double backer and allows combination of double wall board, or 30 pt. liners at higher rates of speed.

Not all of the many advantages reported are found by every user but the following have been suggested. The lower moisture content may mean 20% lower moisture loss requirement for set. This may allow as much as 25% increased machine speed and lower heat input into the drying section. It may result in shorter setting times permitting more rapid use of the product and the use of more fully automatic equipment. Papers with higher moisture content or papers below standard for other reasons may be used to better advantage. The lower alkali content of such adhesives limits staining of blue or green dyes and mechanical pulp. Cases of satisfactory storage of finished board for over a year have been reported. The better bond, flatter board, avoidance of "washboarding" result in reduction of waste. These and the change in adhesive properties may result in economy of consumption and decreased build up on fingers and plates. A reduction in spread from 17-18/M to 11-12/M has been reported.

The greatest influence of the clay addition is on the rheological characteristics of the silicate solution ⁴³. HOUWINK ¹⁰⁹ has reviewed the fundamental properties of clay dispersions. Without clay the solutions behave



Fig. 109. Mixing unit for the manufacture of sodium silicate-clay adhesives showing the mixing pump and storage tanks for continuous preparation.

essentially as truly viscous liquids. With clay they exhibit marked plasticity as shown in Fig. 110²⁴. In Fig. 111 is shown the effect on gel strength

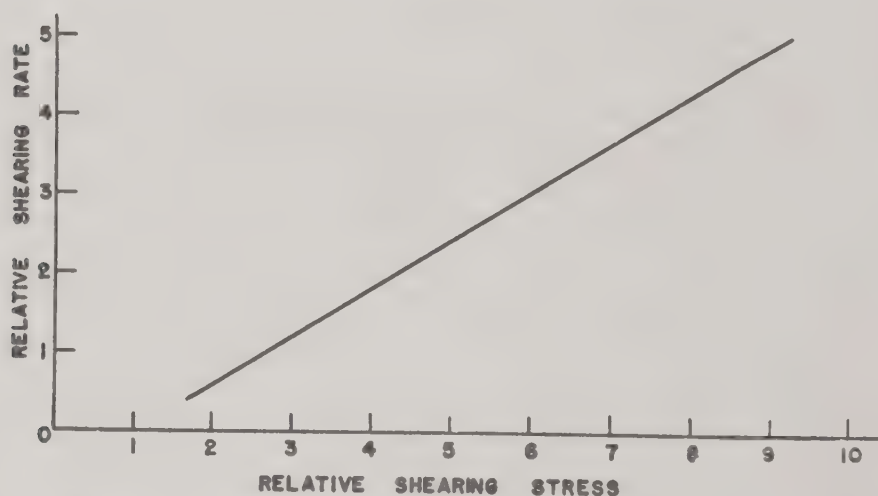
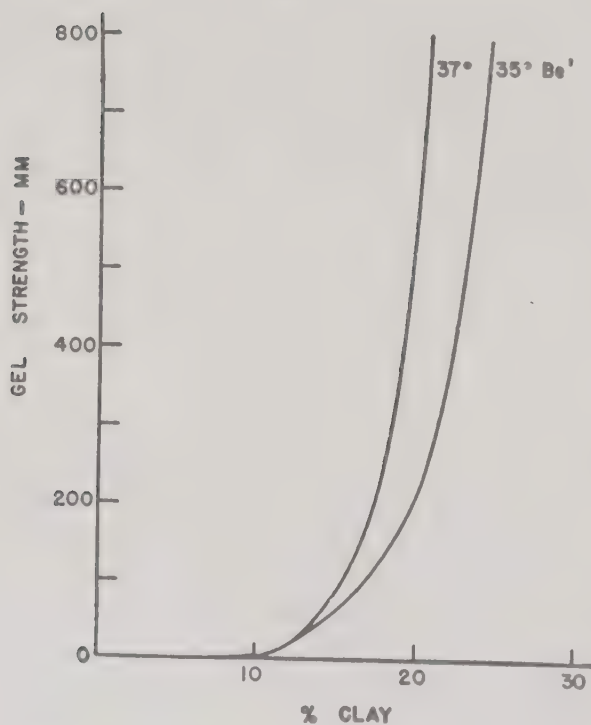


Fig. 110. Plasticity of suspensions of Kaolin clay dispersed in sodium silicate adhesive solution as shown by the relation of shearing rate to shearing stress (BOLLER, LANDER and MOREHOUSE.)



measured in mm of increased length of a Jolly balance when a constant speed motor was used to lift a wire screen through the adhesive solution⁴⁰.

Clay-silicate mixtures may be prepared by the supplier or in the individual plant by the use of a high pressure pump which discharges the liquid silicate through a nozzle. This nozzle draws clay from the charging hopper

Fig. 111. Increase in gel strength of suspension of Kaolin clay in an Na_2O , 3.32SiO_2 adhesive solution at room temperature and a final gravity of 35° and 37° Baume as measured with a Jolly balance.

and develops a strong mixing action which effectively disperses the clay.

Carefully prepared clay-silicate adhesives show very little settling or "bottoms". They can be shipped over long distances and stored for as long as a month or even more. If desired however, the clay can be protected against settling by incorporating an alkali metal soap, e.g. 0.05%–0.10%

for 7% to 10% clay. If too much soap is used, a creaming will result ⁴⁰ but with proper preparation, no separation occurred in about two months.

The preparation and properties of the commercial clay-silicate adhesives are described in patents to VAIL and BAKER ¹¹⁰ and BOLLER and REMLER ¹¹¹. VAIL and BAKER found that the preparation of the initial dispersion could be made easier by first adding peptizing or deflocculating agents which might be a small percentage of sodium silicate, such as 0.1 to 10% of the clay-water mixture. This latter might contain 60% of clay. The bulk of the sodium silicate could then be added to the clay dispersion without causing flocculation of the clay if suitable mixing was provided. This method triples the viscosity and quadruples the gel strength and reduces the settling of the clay to 0.10 compared to a

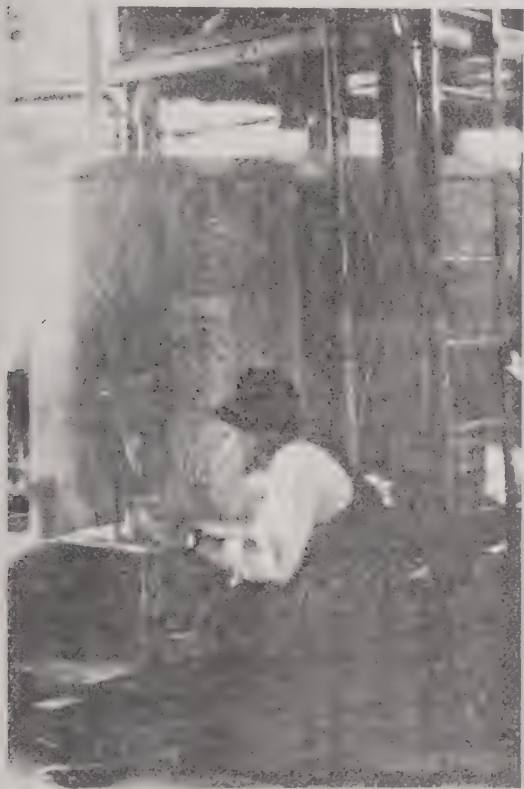


Fig. 112. Plant control of the viscosity of sodium silicate-clay adhesives using a Marsh funnel test—adapted from oil field techniques.

clay-silicate prepared without preliminary deflocculation.

They also stated that the adhesive could be improved by a short heat treatment at from 50 to 165° C. This would bring about partial solution of the more reactive portions of the clay giving a more stable suspension and reducing the clay necessary to give the proper characteristics.

VAIL and BAKER form the silicate-clay adhesive as "a substantially stable suspension having an aqueous phase with the viscosity falling on the low viscosity side of the 'knee' of the viscosity-specific gravity curve". (Fig. 95). They used the more dilute liquid phase to wet heavily sized water repellent

surfaces more rapidly. A clay content of less than 20% was used to increase the thixotropy and thus decrease penetration.

"The viscosity and gravity of the resulting adhesives can be adjusted within proper limits by properly choosing the clay, by control of the amount of clay added and by varying the concentration of the silicate." The finished adhesive should have a viscosity of 140–180 cp for best results but as high as 250 cp has been used. They also suggest that the adhesive should have a filtration volume * within the range of 4–15 cc. ^{34, 43} Such adhesives allow control of penetration and are less sensitive to the moisture content of the paper.

A representative composition was given as 400 pounds of water mixed with 5 pounds of 41° Bé Na₂O, 3.22 SiO₂ solution. 550 pounds of china clay were dispersed therein and subsequently 5,545 pounds of the same sodium silicate solution were added with constant stirring. This produced an adhesive having an apparent viscosity of 140 cp and a filtration test of 9 cc.

The clay used should usually be kaolin, 97% through a 325 M screen. It must be readily dispersible in concentrated sodium silicate solutions and the viscosity of the mixture should not increase more than 20 centipoises in one month. Materials which react chemically with the silicate will result in marked increases.

The adhesives of BOLLER and REMLER ¹¹¹ are essentially similar. Their method was to add a clay water dispersion to a rotary pressure dissolver containing the required amount of sodium silicate glass, clay and water to give 3–15% clay. Temperatures in the range of 138–145° C (50–60 pounds gage pressure) should be used.

BOLLER and REMLER determined a yield value, a coefficient of mobility, a thixotropy ratio, and a stability ratio to characterize their products.

A representative adhesive contained 4.1% clay, 26.7% silicate solids, and had a stability ratio of 1.5, a yield value of 32 dynes/sq. centimeter,

Time	Force of separation	
	Prepared Adhesive	Ordinary 40.5° Bé Na ₂ O, 3.22 SiO ₂ adhesive
30 seconds	25 oz	24 oz.
60 "	34 "	30 "
90 "	37 "	28 "
120 "	38 "	31 "
180 "	51 "	38 "

* Filtration volume is determined by measuring the effluent of 40 cc of the adhesive in 24 hours using a No. 40 Whatman filter paper in a long stemmed 60° funnel.

a mobility of 0.33 Rhes and a thixotropy ratio of 1.3. The rate of set of this mixture, determined by the force in ounces to pull a liner 3" wide from a corrugating medium of the same width after a specified time, was compared to a normal silicate adhesive.

With the straight sodium silicate a water loss of 15% is necessary for initial set. This is just sufficient to permit slitting, scoring and handling at the take-off and the final bond is obtained during seasoning in the pile. As a comparison, the average 10 pounds of sodium silicate used on the double backer must lose 1.5 pounds of water for initial set before reaching the take-off; the cold silicate clay mix requires only 12½% moisture loss or about 1.4 pounds for initial set⁴³; the hot clay silicate mix requires a loss of only 7.5 to 10% for initial set or less than 1 pound before reaching the cut-off.

Much of this loss with the hot clay-silicate adhesive is a "flash" evaporation occurring as the adhesive is applied to the board. This flash is not obtained until the temperature of the adhesive is about 150° C or higher. At 185° F the flash may be nearly 5%. These clay-silicate mixtures used hot are very viscous at room temperatures but have the proper working viscosity at the temperature of use. The addition of clay not only aids in the handling characteristics and reduction of moisture loss but also makes it possible to use a more dilute liquid phase which lessens the tendency to skin on the rolls and in the pan.

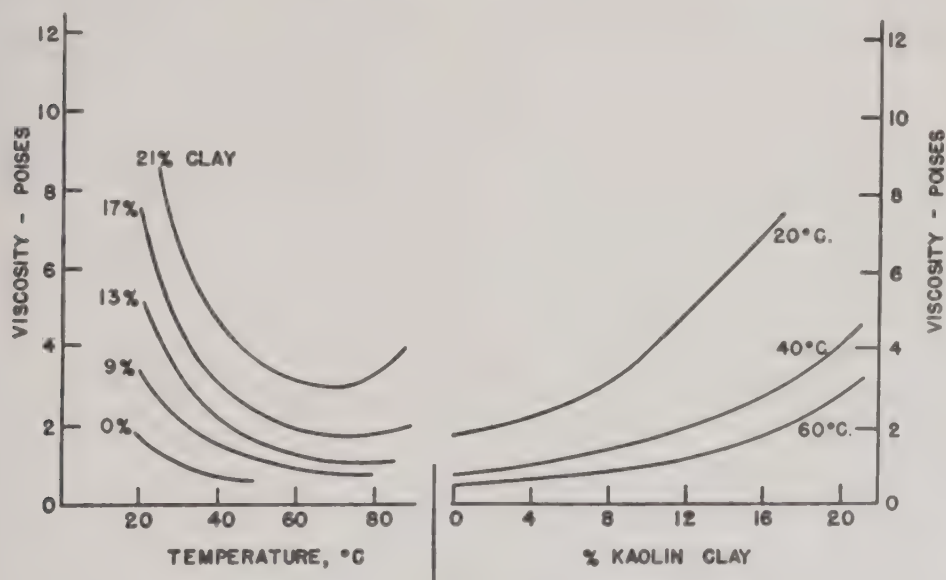


Fig. 113. The relationship of viscosity, temperature, and clay content in a sodium silicate adhesive with an $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of 3.4 as determined by a Brabender Viscograph (KREYLING).

At temperatures of above about 170° F the viscosity of these adhesives again begins to rise (Fig. 113). This viscosity increase appears to be reversible. Advantage may be taken of the viscosity rise by using liners which have been preheated to the usual temperatures of 230° F or thereabouts. By a combination of flash evaporation and increased viscosity at higher temperatures an initial set may occur, theoretically, without appreciable loss of moisture into the liner boards. Long hot plate and cooling sections are not required to produce a flat board ready for the subsequent operations of box production.

The hot clay-silicate where applicable has the further advantage of substantially increasing the speed while maintaining a better bond. For instance 30 pt. and double wall combinations may be manufactured at rates usually obtained only with regular test board. Substantial reductions of hot plate and cooling sections may be made and yet permit fully automatic handling. One of the major advantages is that the board calipre may be increased by 0.003 to 0.080" because of the reduced crushing of the flutes under the weight of the rolls. The drier boards better resist such loads. The increased calipre permits sharper scores and results in straighter folds.

Advantages of the hot clay-silicate system may be utilized by a box maker who binds substantial amounts of heavy calipre or double wall board or who has a serious warp or folding problem. Alternatively he must be willing to make the mechanical changes necessary to increase production substantially¹⁰⁸.

(e) *Engineering Characteristics of a Good Bond*

The picture of a man standing on a completed box (Fig. 114) made with a silicate adhesive six minutes after the liner and corrugating medium were fed into the single face station illustrates very graphically the rapid formation of a strong bond.

MCCREADY and KATZ¹¹² show that boxes made with silicate of soda adhesive may well be 10 or 15% stronger than those made with competitive adhesives. "The only differences in the fiber board and the boxes were in the type and amounts of adhesive used." They summarized the pertinent test data as shown in Tables 35 and 36 and as follows:

"1. The MULLEN test of fiberboard does not evaluate the board in a way comparable to the compression strength of boxes made from the board. The reverse is indicated in these data, in that the boards having the greatest MULLEN test values produced the weakest boxes.

2. The structural tests on the fiberboard, that is, evaluations by column and beam loading, vary in test values in a manner similar to the compression strength tests of the boxes. The values obtained with these tests on fiberboards are indicative of the compression strengths of the boxes made from the boards.



Fig. 114. A corrugated box six minutes after the paper was fed into the corrugator.

3. The four boards made with silicate adhesives and the boxes made from these boards were, structurally, considerably stronger than the similar boards and boxes made with the starch adhesive.

4. The use of heavy applications of silicate adhesives increased considerably the structural strength of the fiberboards. No equal benefits resulted from the use of heavy applications of the starch adhesive.

The structural data obtained on the corrugated boards have been theoretically correlated with the structural properties of boxes. The modulus of elasticity of fiberboard, which is an expression of its stiffness, has been used to predict the compression strength of boxes, with sufficient success so that the modulus may be considered to be indicative of box strength."

In a later paper MCCREADY¹⁰³ gives the results of the series of tests on the stiffness of comparative board. (Table 37). He says, "The influences (on stiffness factors) of the adhesives were revealed

and in most instances the adhesives appeared to have greater influence on the physical properties of the corrugated board than any other factor with the exception of poor fabrication."

"In the formulation, of most structures the modulus of elasticity and moment of inertia are found together as EI , which in this combined form may be considered as a stiffness factor . . . it may be used as a means of evaluating fundamental physical properties of corrugated board . . . the boards made with silicate and silicate-clay adhesives in most instances had about the same stiffness, and the boards made with either of

TABLE 35

PROPERTIES OF "A" FLUTE CORRUGATED PAPERBOARDS AND BOXES TESTED
BY MCCREADY AND KATZ

Board- adhesive application	MULLEN Test lbs/in. ²	Structural Tests on Paperboard Beam Loading				
		*Compression Strength of Boxes, lb.		Column load lbs.	Breaking load lbs.	Deflection at constant load 2.8 lbs/in.
		Top to Bottom	End to End			
Silicate-Normal	226.8	1021	765	171	4.9	0.431
Silicate-Clay-Normal	232.6	1082	777	194	5.2	0.413
Starch-Normal	243.6	916	729	153	4.5	0.546
Silicate-Heavy	210.2	1229	794	209	5.7	0.387
Silicate-Clay-Heavy	219.2	1074	787	222	6.0	0.345
Starch-Heavy	244.7	899	677	161	4.3	0.586

Tests on paperboard at 70° F and 50 % Relative Humidity.
MULLEN tests single face up.

Column Tests — 4" × 4" samples; corrugations vertical.

Beam tests — center loading, 3" × 12" beam, corrugations parallel
to beam length, single face up.

the silicate adhesives were stiffer than the boards made with starch adhesives."

The effect of the adhesive on the critical load is shown in Fig. 115 for a kraft-straw combination in a column test with corrugations vertical.

TABLE 36

EXPERIMENTAL AND COMPUTED COMPRESSION STRENGTH OF CORRUGATED
PAPERBOARD BOXES (MCCREADY AND KATZ)

Board		Computed Strength in Pounds		Experimental Strength top to bottom
Adhesive	Application	Column Modulus	Beam Modulus	
Silicate	normal	1021	1021	1021**
silicate clay	"	1115	1063	1082
starch	"	910	817	916
silicate	heavy	1235	1030	1229
silicate clay	"	1324	1160	1074
starch	"	965	790	899

* Box Compression Strength Data from D. L. Quinn Company, Chicago, Illinois.

** This board was used as the standard.

References p. 344

Flexing tests showed that where board was properly formed "those boards manufactured with silicate and silicate clay adhesives withstood a much greater number of flexes." "The results of the flexing test indicate that the fatigue resistance of corrugated fiberboard is closely related to ultimate strength. The separate test pieces gave widely varying results and it is considered that flexing tests magnify the effects of poor fabrication."

Table 38 gives data obtained with well formed sheets.

In line with the data of engineering value * obtained by MCCREADY and KATZ¹¹² is the information on the actual bond structure as shown by SCHUPP and BOLLER⁵¹ and BOLLER, LANDER and MOREHOUSE²⁴. Both papers show pictures of good and bad bonds and discuss the reasons for the differences observed. BOLLER *et al.*, Fig. 116, shows "Photomicrographs taken at magnifications of 22 and 144". "In general its strongest bonds are those which approach closely the configuration shown . . ."

The thick layer at either side of the contact bond is called a shoulder. The thin portion extending along each paper surface beyond the shoulder is a reinforcement. The shoulders sometimes are hollow forming a truss structure. In any case it may be concluded that a well formed bond has characteristics of an engineering structure designed to give the greatest possible support to the flute and the bond. The width of the adhesive strip should be from 1 to 2 mm and penetration should be about 0.0025 to 0.0050 mm (0.001 to 0.002"). Greater penetration usually accompanies loss of shoulder formation and results in a brittle bond. Use of excessive

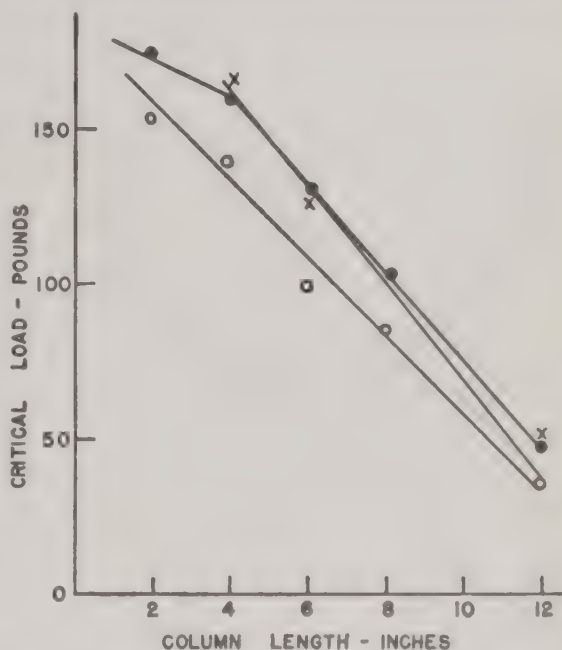


Fig. 115. A comparison of the critical load withstood by columns of "A" flute board with vertical corrugations when bonded with normal spreads of:

- commercial sodium silicate adhesive (3.3 SiO_2 : Na_2O and 41.5° Bé at 60° F).
 - × a suspension of Kaolin clay in a sodium silicate solution of the same ratio.
 - a standard starch mixture used as a corrugating adhesive.
- (D. W. MCCREADY).

* Refer also to Chap. 4, sections 5 and 11 for a mathematical discussion of stress relationships in bonds formed with flexible adherends.

spreads to compensate overpenetration may, under favorable circumstances of storage, result in staining”.

“When corrugated boxes are subjected to compression tests, the failures invariably start at the breaks or points of weakness in the adhesive bond.”



Fig. 116a.

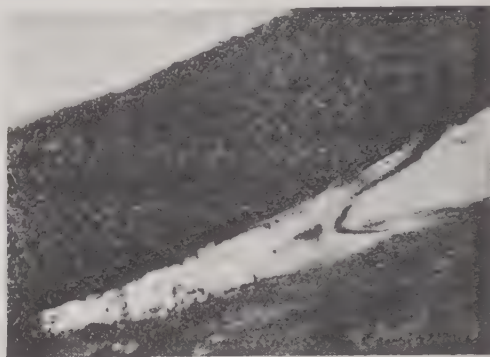


Fig. 116b.



Fig. 116c.

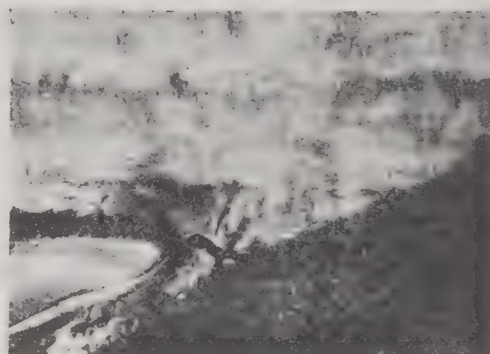


Fig. 116d

Fig. 116. Fresh silicate bond sectioned in Canada Balsam. a-b: Double backer bond with silicate adhesive between corrugated and flat sheets. c-d: Single facer bond with silicate. Corrugated member depressed below liner surface. (BOLLER, LANDER and MOREHOUSE).

Points of weakness of the bond may be traced to improper machine adjustments which do not permit the formation of complete glue lines of the required structure.

Such matters of operating technique affect all adhesives and can be controlled by adequate training of the operators. Build-up on the hot plates also can be minimized by proper control and can be made of small moment by the addition of specific organic materials such as rosin-maleic anhydride condensation products, triethanolamine or alkyl aryl sulfonates¹¹³.

TABLE 37

STIFFNESS FACTORS EI DETERMINED BY McCREADY FOR 1" WIDE COLUMNS
WITH VERTICAL "A" FLUTE CORRUGATED BOARD

Column Length	4''	6''	8''	12''
Silicate *	62.7	91.0	154	129
Starch *	54.7	88.2	127	107
Silicate-clay **	67.5	116	167	139
Silicate **	65.2	118	168	160
Starch **	57.1	91	139	129
Silicate *	55.0	94.0	157	159
Starch *	45.0	61.3	105	111
Silicate ***	69.7	122	156	139
Starch ***	59.1	94.6	125	107

SCHUPP and BOLLER, Fig. 117, in an interesting series of X-ray photographs which will repay careful study have correlated bond structure of the single face and double face bonds with machine characteristics and adhesives. They find that variation in the properties of the adhesive has little effect at the single face bond except at extremes of viscosity or body. Use of minimum silicate will usually reduce the bond strength below that of the double face bond and a tendency for the shoulder to form on one side onyl is greatly increased.

In the case of the double face bond, too fluid an adhesive causes loss of shoulder structure and the bond is much more susceptible to imperfections traceable to machine characteristics. Increased body in the adhesive usually

TABLE 38

FLEXURE TESTS ON "A" FLUTE CORRUGATED PAPERBOARD
Rate of Flexure — 40 cycles per min (McCREADY)

	Ultimate load	Flexing load lb.	Percentage of ultimate	Number of flexes
Silicate *	4.56	4.0	87.5	10,000+
Starch *	4.12	4.0	97.0	37
Silicate clay **	5.59	3.65	65.2	10,000+
Silicate **	5.69	3.65	64.0	10,000+
Starch **	4.29	3.65	85.0	2,090

* Kraft liners, chestnut corrugating medium
** Kraft liners, straw
*** Jute liners, straw

overcomes such machine deficiencies and allows formation of adequate shoulders.

In general, too, they found little effect of paper on either bond structure

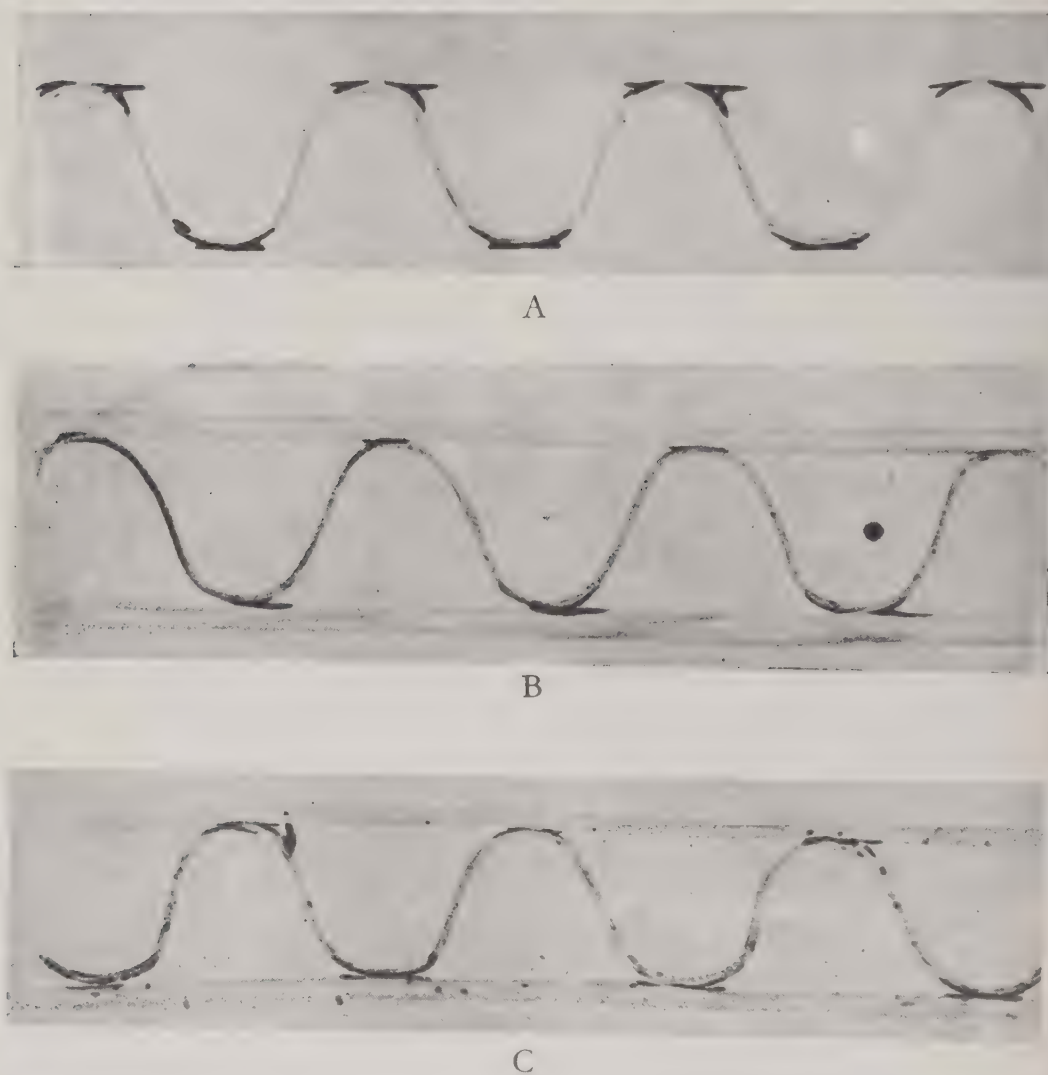


Fig. 117. Cross sections of corrugated board by X-ray examination.
(Courtesy E. I. du Pont de Nemours & Company)

- A. Normal bond.
- B. Starved bond.
- C. Thin adhesive.

or penetration. Where excessive penetration did occur it appeared to increase the compressive strength of boxes made therefrom. MCCREARY¹⁰³ also noted that impregnation of the medium seemed to increase compressive strength of the product.

(f) *Mechanical Waste*

Waste in some specific cases has been investigated carefully by BOLLER *et al.*²⁴ They found that where the total waste averaged 3.7% only 0.25% could possibly be attributed to characteristics of the sodium silicate adhesive. These factors were "blisters on single face (dirty corrugating rolls), fingers too close to edge of sheet, miscellaneous."

Another cause of waste is warp. If severe it may prevent the use of the



Fig. 118. Board to the left illustrates "wash board" appearance often found where liner has been subjected to adhesive with high water content. Flat board to the right made with silicate adhesive.

sheets entirely. A single sheet will warp when wetted because the percent change in fiber diameter is greater than that of the fiber length. The fibrils generally lie in the machine direction and the resultant change is greatest across the sheet¹¹⁴. Warp of corrugated board is caused by an unbalanced moisture content in the liners at the time the bond sets. On subsequent drying the contraction causes the board to warp.

Washboarding has a somewhat similar source. It results from a very wet liner stretched across the corrugation. If, in this weakened condition it is stretched beyond its elastic limits, it fails to recover the smooth flat surface when dried. Such a condition is very seldom found when silicates are used as the adhesive.

Silicate introduces such small amounts of water into the liner that warpage is likely to develop only when water from other sources is introduced. This source is usually insufficiently dried paperboard. Board containing 12–15% moisture, a very damp board, has been combined satisfactorily by increasing the viscosity of the usual Na_2O , 3.3 SiO_2 solution to 42.5° Bé from its original gravity of about 40.5°.

High moisture content in the board also is a factor in deformation of the flutes and the consequent reduction in the maximum strength of the finished board product. Paper has its greatest strength at low moisture content. Above about 9.0% H_2O the strength properties fall off along a curve having a shape similar to that of the silicate solution viscosity-gravity curve (Fig. 95). The “knee” occurs around 9% moisture content. This applies directly to flat crush strength of the board. The higher the moisture content of the medium at the double backer the more certainly will the flute be deformed by the pressure section.

(g) *Water and High Humidity affect the Bond*

The effect of water on the paper is to be differentiated from that on the bond itself. Unless protected by a suitable size, usually rosin, paper fibers take up water rapidly by capillary action between the fibers in the sheets ¹¹⁴. When thus wet, paper fibers are very weak and easily separable. Alkalies react with the rosin components and reduce or destroy the protective action.

A sodium silicate bond when cured is only slowly soluble even when immersed in water. A piece of sodium silicate glass for instance will not change appreciably in weight on several hours soaking in cold water although the water in the vessel will rapidly become alkaline. A higher ratio or a mixture with clay reduces the rate of solution. Once thinned out, however, sodium silicate runs off or sinks into the paper and the bond is entirely lost. Compared to other water soluble adhesives sodium silicate bonds are quite resistant to solution.

The magnified view (Fig. 119 a) shows the result of forcible separation of a thin section of a corrugated bond formed with Na_2O , 3.2 SiO_2 adhesive after soaking for twelve minutes. Fig. 119 b shows a clay-silicate bond separated after soaking for twenty-five minutes. Long soaking will of course dissolve the bond completely.

Soaking is analagous to conditions of 100% relative humidity, a saturated water atmosphere. Eventually the bond will become so soft as to disappear in the paper and allow delamination but as the curves of Fig. 92 suggest, the relative humidity must be nearly 100% for this to happen.

One of the worst effects of storage at high relative humidity is the support of the migration of alkali through the paper. Reaction of the alkali with the rosin may not only reduce resistance to water but may

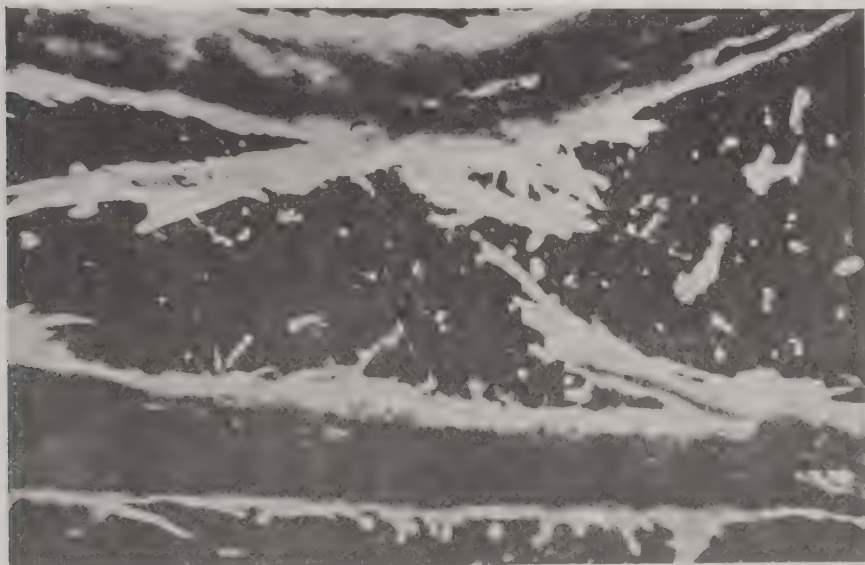


Fig. 119. Thin sections of silicate bonds forcibly separated after soaking in water.
a. $\text{Na}_2\text{O}, 3.3 \text{ SiO}_2$ separated after 25 minutes.



Fig. 119 b. Silicate-clay separated after 25 minutes. Note the truss structure still intact.

change the color of the surface of the liner or the color of the ink used, i.e. "staining".

Experiments with a wide variety of papers and concentrations of silicate adhesives resulted in no staining at a relative humidity of 70% but it did occur at 100%. The time of appearance of stain varied from a week to about a month and was shortest for Fourdrinier Kraft whereas cylinder kraft and jute were scarcely affected¹¹⁵.

The transport of alkali is reduced by decreasing the spread to the minimum required for a good bond, drying rapidly, and using sodium silicate adhesives with a ratio of $3.3 \text{ SiO}_2 : 1 \text{ Na}_2\text{O}$ or preferably higher. It is also preferable to use alkali resistant inks.

The pictures, Fig. 120 and 121, are instructive of the effects of varying the adhesive used. In the first two, 120 a and 120 b, a glass of water has been inverted for 7 and 15 hours respectively

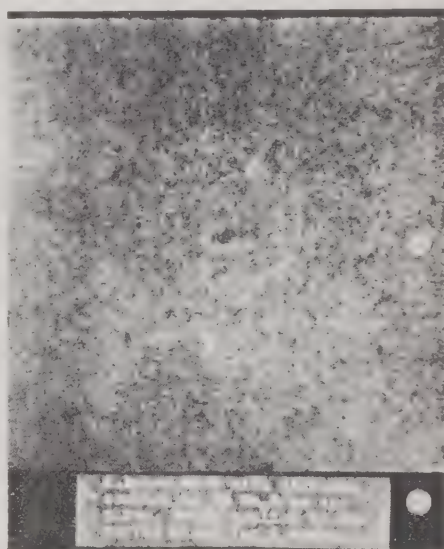


Fig. 120. The transport of alkali through corrugated paperboard.
a. Water applied to outer liner face for seven hours.

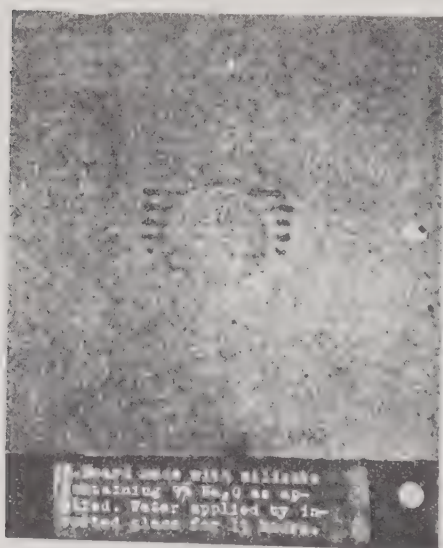


Fig. 120 b. Same after fifteen hours.

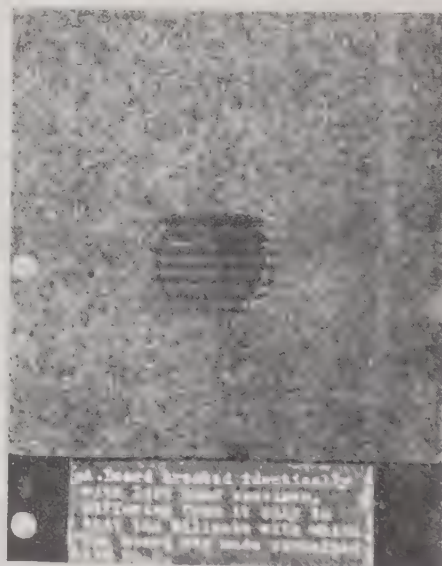


Fig. 120 c. A more alkaline ratio adhesive after seven our test.

over a double face corrugated board made with Na_2O , 3.3 SiO_2 solution containing 9% Na_2O . After seven hours the water had not had time to pass through the liner to the alkali and bring it up to attack the rosin size. Fifteen hours was just sufficient. On the other hand (Fig. 120 c) the board was thoroughly wetted within seven hours when an Na_2O , 2.9 SiO_2 solution at a concentration of 11% Na_2O was used. A safe rule is not to use such an alkaline ratio within one thickness of paper from the outside.

The remaining picture Fig. 121 compares the Na_2O , 3.3 SiO_2 with the Na_2O , 4.0 SiO_2 solution. In this case the samples were first stored over water in a humifier for a month and then given the water test just described for seventeen hours. The greater resistance of the higher ratio is very evident. The lower half of each board shows the result of the same test before aging in the humidifier.

Developments by CARTER have made it possible to preclude staining and to

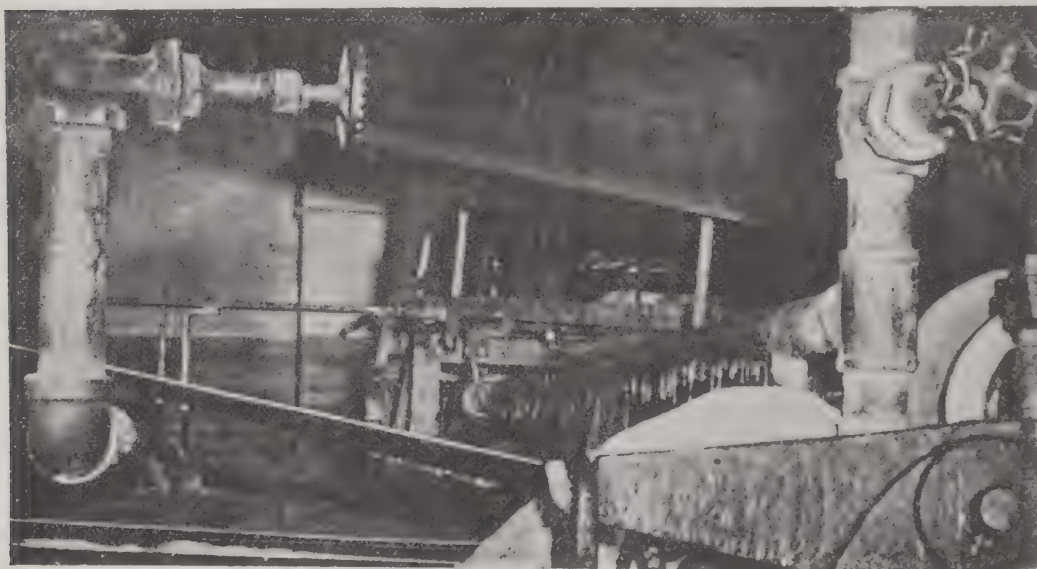


Fig. 121. Comparison of staining by two high silica: alkali ratio adhesives. Left: Na_2O , 3.3 SiO_2 given the inverted glass test with water for 17 hours after storage at 100% R.H. for one month. Right: Na_2O , 4.0 SiO_2 after the same test.

produce a truly water resistant bond using sodium silicate adhesives. Numerous attempts have been made to use mixtures of soluble silicates with salts forming insoluble compounds but these always result in loss of tack and brittle crystalline bonds. CARTER⁸³ found that he could coat one or more surfaces of a liner with a salt which would neutralize the alkali and/or form a gel with the silica. These salts prevented the migration of the alkali to the surface without affecting the formation of the bond. They did not, however, form a water resistant bond although they did aid in resistance to high humidity.

Liners may be coated either before or during operation and indeed board which shows stain may be recovered by a subsequent coating operation. However, the processes are not often needed since the use of higher ratio, more viscous solutions and solutions with controlled clay content restrain the penetration of the silicate so that there is little tendency to stain through. These operations also have given increased resistance to high humidity.

If a really water resistant bond is required the method of CARTER ⁶⁷ may



Courtesy Certain-Teed Corporation

Fig. 122. Application of the adhesive to both sides of an inner ply solid fiberboard.

be employed. He disclosed that aluminum chloride alone or a series of similar salts could be used to form a water resistant bond. The coating solution had to be applied to the surface to be bonded and dried before an effective bond could be produced and the aluminum ions should be balanced against the alkali added by the adhesive. Bonds formed in this way will meet the test of U.S. Specification JAN-108, 1946 for water resistant board.

The explanation of the specific behavior of Al and Cl ions is not known. It is assumed that under the conditions described the alkali is essentially neutralized without the formation of too large gel particles before the bond sets. At the same time it may permit reaction between the cellulose and silica micelles before neutralization reduces their ability to form bonds. Protein-silicate mixtures as water resistant adhesives will be mentioned later.

The effect on silicate bonds of specific gases in the atmosphere is sometimes mentioned. Actually they may have a slight surface effect but there are records of corrugated boxes which have maintained a good bond for 10 years¹¹⁶. Exposure of test pieces for three days at 55% R.H. and otherwise pure CO₂ gave the same bond strengths as when unreactive nitrogen was used¹¹⁷.

§ 10. SOLID FIBER BOARD

The production of laminated solid fiber board is quite old with a history going back at least to 1850. A pasting machine was patented in England in 1824 by JOHN DICKINSON⁷.

Modern machines are limited by the difficulty of drying board thicker than about 0.050" and most solid fiber board is made up to 0.016" with thicker board, up to around 0.250", built up by further lamination or pasting. The usual maximum is 5 plies.

Although as the Table 39 indicates, laminated solid fiber board has not kept pace with corrugated board, it is still in demand where strength and toughness are required without the shock absorbing properties of a corrugated structure. About 111,425 short tons of chipboard were so used in 1946. Most of the famous water resistant V-board used in the last war was solid fiber.

TABLE 39
COMPARISON OF THE CHANGES IN THE PRODUCTION OF CORRUGATED
AND SOLID FIBER PAPERBOARD IN THE U.S.A. SINCE 1916

Year	Corrugated Board			Solid Fiber Board		
	million sq.ft.	ave. rate * ft./min.	average * spread in lbs.	million sq.ft.	ave. rate * ft./min.	average * spread in lbs./gluc line
1916	40	50	18	30	75	25
1920	55	65	15	30	125	20
1930	140	200	13	44	200	15
1940	356	300	9	28	300	11
1946	574	350	9	24	350	9

The specifications for solid fiber board boxes used in shipping via railroad are covered in B.S. 1133, Rule 41⁹⁵ and other specifications. They call for similar strength properties whether solid fiber or corrugated paperboard is used.

* These figures are very rough estimates to show the trend of practical limitations.

While paper and spreads used for solid fiber lamination are of the same general nature as those used for corrugating, much higher adhesive viscosities and machine pressures are usually used. Instead of a viscosity range of 1 to 2 poises, "pasters" use about 2 to 5 poises and increase the pressure to about 800 lbs./sq.in. Thus entirely different machinery is required for most efficient production. Originally the plies were drawn through a bath of silicate of soda and excess adhesive was squeezed out by the heavy rolls. As many as seven plies may be laminated at one pass through the machine. They produce a stiff, hard board which must be dried in the stack as all water loss is evidently into the paper and loss to final set is fairly slow compared to corrugated board. The time for initial set as indicated by machine speed and length is 15 sec. or less.

This method of production was satisfactory with the hard smooth chip filler used before 1930 and the introduction of Fourdrinier liners with bulky rough finished chip filler. Such a paper absorbs nearly double the ordinary spread and results in the migration of the alkali through the board, slow drying, and staining.

Besides the use of higher ratios and clay-silicate mixtures it was found that the use of transfer rolls allowed a reduction in the amount of adhesive per glue line to as low as about 6 lbs. per 1000 ft. of single glue line. Even at 11 lbs., discoloration and desizing does not occur with 0.016" plies. The tendency is therefore to use this type of multiple glue stations.

The developments by CARTER^{67, 83} are particularly useful for solid fiber production. Besides protecting the liners against staining and desizing by excess alkali and/or producing a water resistant bond the rate of set is considerably increased. This factor is particularly important in solid fiber production where no heat is used and boards must be stacked to dry before forming into boxes.

§ 11. SEALING

The sealing of paper box-flaps is a laminating process requiring still different adhesive properties and operations. The adhesive chosen depends on whether hand or automatic spreading and pressure systems are used as well as on the liner surface properties, time of set, and later handling.

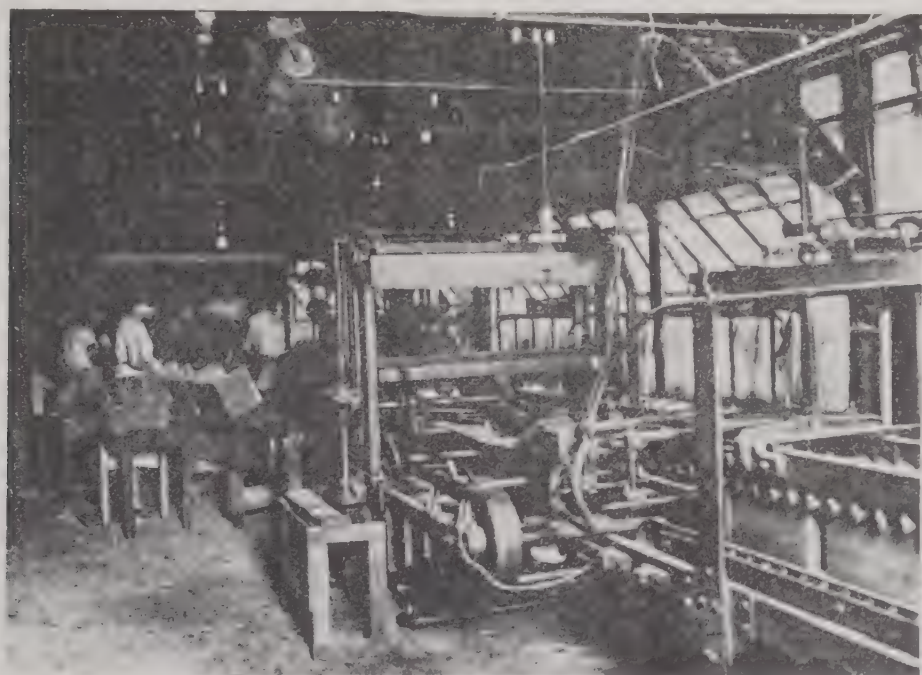
A more tacky adhesive is usually needed for hand sealing and a 1Na₂O, 2.9 SiO₂ solution at 47° Bé is recommended. About 0.011 lb. per square foot is usually brushed over one flap and the flaps are held in contact for 1 to 5 minutes with a pressure of 50 lbs. It is necessary to avoid surface drying before the flaps are closed. As usual, dilution will be needed where

the surface is hard to wet and the time required for set will depend on the spread and the paper surface.

Hale of Forest Products Laboratory¹¹⁸ studied these factors and their effect on the bond strength. He found that in his case there was seldom any adhesive failure after five minutes but that residual moisture in the bond and paper surface prevented the development of full strength for 1 to 4 hours. However, 80–90% recovery occurred in 30 minutes or less. His results were rather erratic, probably because of uncontrolled spread.

Automatic sealing has steadily increased in volume. In these machines the adhesive is applied by transfer rolls and pressure sections allow 1 to 2 minutes for setting after which the boxes may be subjected to rather violent treatment in extreme cases. As in corrugated board production, where good practices are followed silicate adhesives are satisfactory and economical. It has been estimated that they are used in about one third of the automatic sealers in the U.S.A.

These machines may use either the 47° Bé, 1 Na₂O, 2.9 SiO₂ usually used for hand-sealing but here diluted by 8 to 15% of water, or in some cases the less tacky but faster setting Na₂O, 3.3 SiO₂ solution. Spreads as low as 5 lbs/1000 sq. ft. of flap surface have been used to give results comparable



Courtesy Tygart Valley Glass Company

Fig. 123. Full automatic sealer using silicate of soda.

to dextrin glues. As in the case of other applications, the introduction of new papers has made advisable the use of clay-silicate adhesives for some installations. This gives the advantage of adequate wetting with high viscosities. Very thin spreads are often found to give best results where the tack is sufficient. The thixotropy of such mixtures also helps to avoid a chance that adhesive may drip into the contents of the container.

Glued flap boxes hold their shape better than taped boxes when

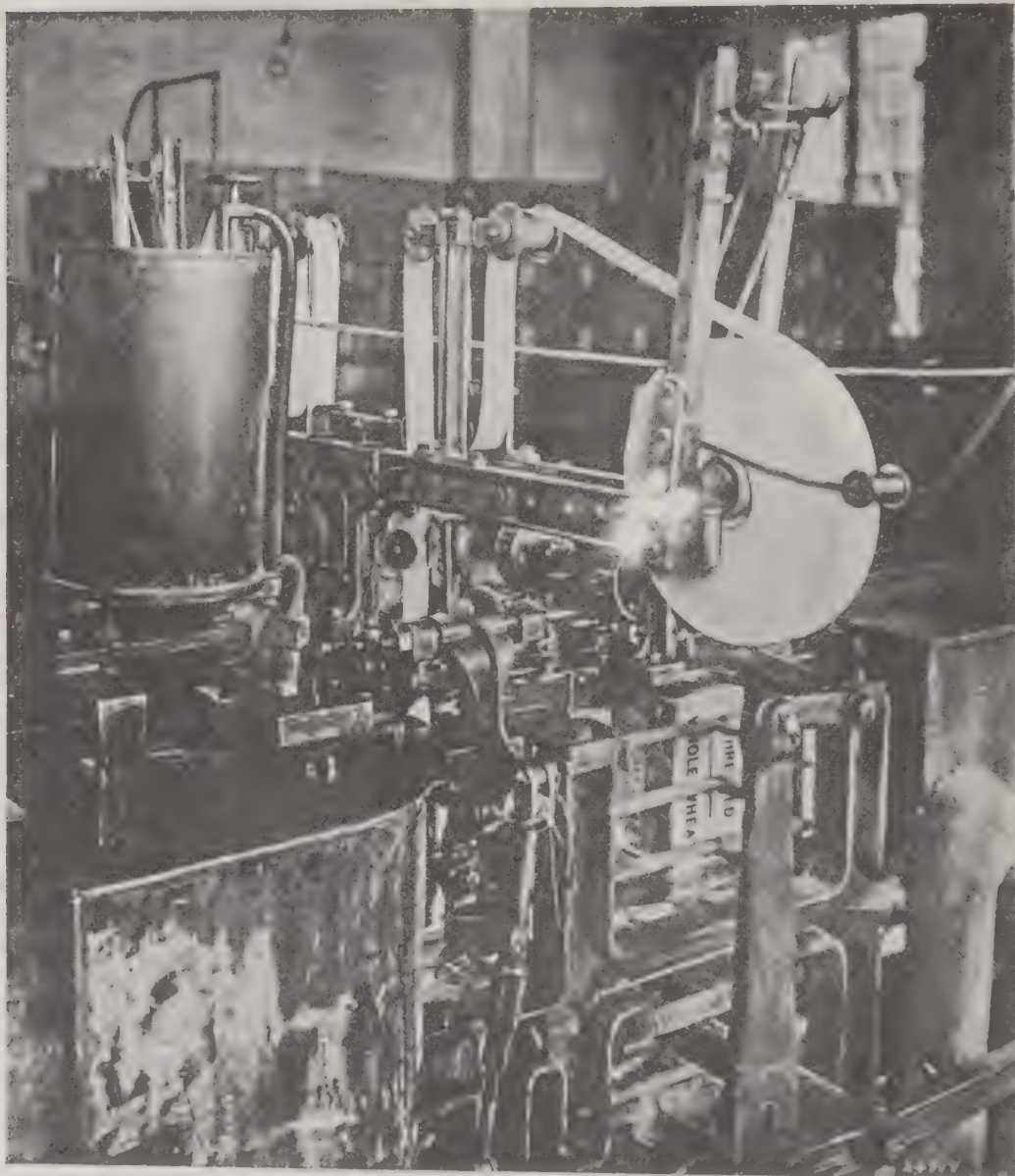


Fig. 124. Sealing cartons of breakfast food with paper tape. Silicate adhesive is applied to the tape.

References p. 344

subjected to endurance tests. One advantage of sealing with silicate is that the bond cannot be separated and resealed without destroying the flaps.

Where, however, the cases are to be stored in refrigerated rooms as near solid CO_2 , special seals may be needed to prevent reaction with the alkaline bond. The high relative humidity is probably responsible for any deterioration.

Where there is trouble with a build-up of silicate on some parts of the machine, the parts should be wiped with a wet rag or may be coated with a bakelite or bakelite-graphite resin lacquer. If this is allowed to dry for several hours it forms a hard impervious film from which sodium silicate may be easily removed.

Various complex mixtures of soluble silicate with rubber, and Portland cement, etc. have been suggested to give faster set or closer control over the tack and final strength¹¹⁹.

Silicate adhesives are used to bond parquetry flooring squares to paper sheets, for capping rolls of toilet tissue and newsprint, and for bonding sheets of paper and metal foil.

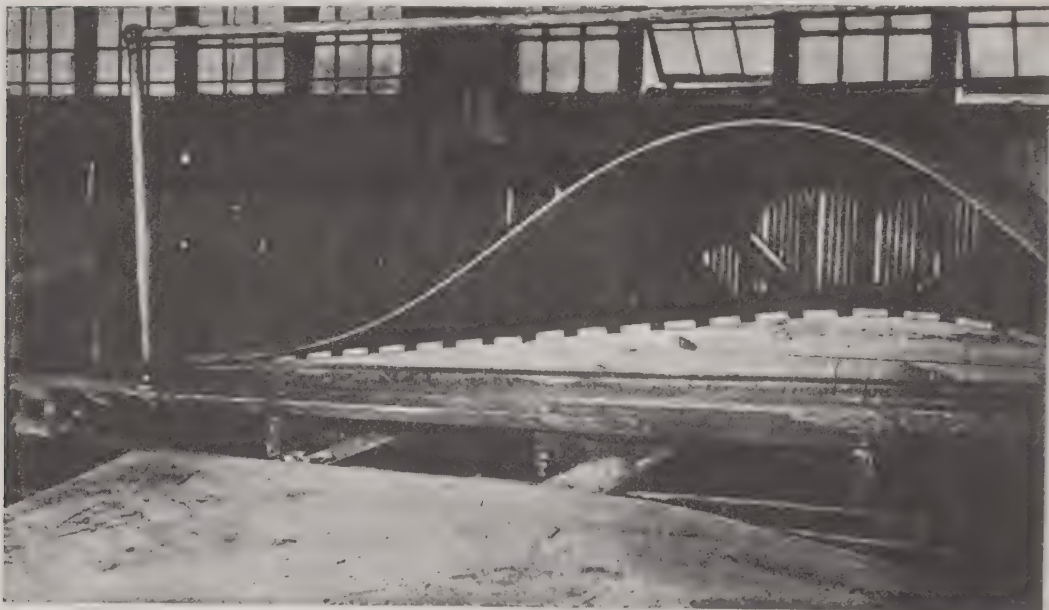
§ 12. LABELING

For pasting labels on containers, the less alkaline higher ratio silicate are usually preferred. Under conditions of unusual dampness, sensitive colors may be affected by the alkaline ratios even though the adhesive did not reach the face at the time of application. Inferior papers may also be discolored by this slow penetration by alkali. The higher ratio more silicious silicate solutions also set more rapidly and maintain their grip under damp conditions.

Surfaces of glass, paper, wood and cardboard are best suited for attaching labels with sodium silicate. A mixture of 100 parts of Na_2O , 4.0 SiO_2 solution and 20 parts of sugar diluted as required has been recommended for labels on wooden barrels². Sometimes additional protection may be obtained by spreading a thin film of silicate of soda over the label after it has been made fast to the package. It will prevent loss of readability by abrasion in transit but is not recommended for articles which may be stored for long periods.

While Na_2O , 2.0 SiO_2 solution has been used to apply labels to clean tinned surfaces, WEGST⁴⁰ has found that the addition of 5% rosin added hot with an equal weight of water improved flexibility, tack and clean-up. A higher ratio containing 8% clay and 3% rosin was also recommended.

The bonding of a silicate layer to a surface of urea formaldehyde may be accomplished by applying the silicate before the high polymer has set to a "fully water-insoluble" state ¹²⁰.



Courtesy Certain-Teed Corporation

Fig. 125. Finished wallboard passing under the cut-off knife of the laminating machine.

§ 13. WALLBOARD

Wallboard building boards made by lamination of paper were developed about the time of the first world war. Although they have been outstripped by newer forms of building board, about 47,500 short tons were produced in the U.S. in 1946 ⁹³. The use of thick highly absorbant chip filler stock, slow drying time and the slow setting speed required development of a special adhesive for continuous formation. CARTER ¹²¹ and THICKENS ¹²² disclosed silicate adhesives containing clay in the range of from 25–40%. This clay was not as well dispersed as that in present day fast setting clay-silicate adhesives and the method of application allowed the use of a thick creamy consistency. The clay acted as a dam against seepage of the adhesive into the stock and reduced the water loss required for set while allowing the use of a diluted liquid phase which did not readily skin over or set before the paper had passed through the machine.

Water resistant bonds for laminated paper board have been described by CARTER ⁶⁷. A mixture of a more alkaline ratio silicate with finely divided whiting has also been used for wallboard. Not all supplies of calcium

carbonate have the proper reaction and they must be checked before use. A bond of 25 parts of $1\text{Na}_2\text{O}$, 2.0SiO_2 solution at 60°Bé , 25 parts of water and 60 parts of whiting becomes insoluble in about a week but it will still be weak when set. For lamination of wood a more silicious silicate must be used (see § 16).

Lamination and sealing are also factors in the formation of other types of building board. 251,956 tons of paper stock were used in the U.S. in 1946 to coat gypsum and plaster board. In general the reaction of the sodium silicate with gypsum causes the paper lining to separate and other adhesives are used. The lap of the paper envelope covering the gypsum is usually sealed with a heavy $1\text{Na}_2\text{O}$, 3.3SiO_2 solution having a gravity of about 42°Bé .

In tropical countries laminated wallboard made with sodium silicate has been found to be an effective barrier against ants and other cellulose-consuming life¹ (see § 5e).

§ 14. FIBER TUBES, CANS AND DRUMS

These paper containers are yet another example of lamination with peculiarities which require specialized equipment and adhesives. Tubes and cans

are generally considered as having a diameter of less than 6" although most are made in diameters of 3" or less. A can is merely a tube equipped with ends and a label. A drum has a diameter of 6" or greater. Tubes are produced continuously at speeds of 240–300 fpm which are equivalent to paper speeds of 90–100 fpm. Drums are produced more slowly and with semi-automatic equipment. A medium tack, fast setting sodium silicate adhesive with a ratio of $1\text{Na}_2\text{O} : 3.4\text{SiO}_2$ is usually used in drum fabrication.

Tubes are made by the convolute (straight wound), spiral wound, or lap seam method. Convolute tubes having a diameter greater than



Fig. 126. Spray gun application of paper and adhesive as an insulation.

2" are usually made with sodium silicate adhesives. The spiral wound tubes are made at higher speeds and ordinarily require special provisions to take advantage of the economy and rigidity of sodium silicate. A tube having a diameter of about 3" may be made with sodium silicate if the mandrel is lengthened to provide the longer setting times required to prevent "dog ears" (delaminated points) which may occur at the pointed end of the ply or if proper allowances are made for changes in relative humidity.

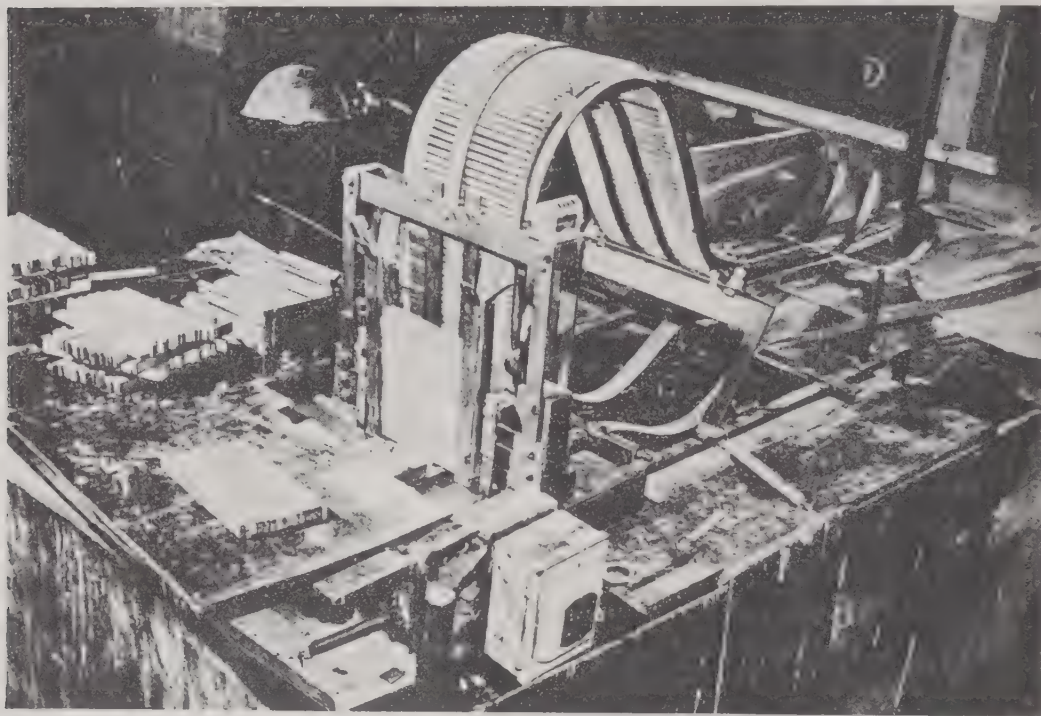


Fig. 127. The application of felt to wood.

The adhesives should have a high viscosity and may also be formulated with clay or whiting to control the body, tack and setting time. The thinnest possible spread is often found most satisfactory and special scrapers may be installed to reduce the spread to less than 20 pounds per 1000 sq. ft. of glue line. For news-stock sized with sodium silicate and alum, a setting time of 8 sec. was observed on a 5" diameter tube.

§ 15. INSULATION, ETC.

Various fibrous materials have been bound together and to a backing to form heat, sound and electrical current insulation. While no really new principles are employed it is of interest to survey a representative list.

(a) *Paper, etc.*

Fragments of paper bound to wood, paper or metal backing have been used as insulation and cushioning. Wool felt and cotton filters have been formed. Silicate was used as a combination adhesive and fireproofing agent in lining jute bats ¹²³.

Light solid sheets have been formed from wood fiber, from seaweed, from cork. HAKANSON ¹²⁴ found however that the cork needed to be treated first with strong alkali.

Ceiba or kapok could be glued to muslin if the sodium silicate was first drawn or forced into a shallow layer of the kapok ¹²⁵.

REACH ¹²⁶ took advantage of the slow rate of solution of the dried film to form cleaning swabs from cellulose base materials.

(b) *Asbestos*

Asbestos insulation against heat and sound is built up in divers forms by lamination with heat resistant adhesives. Sodium silicate is usually chosen where the temperature of use is less than 370° C but is generally satisfactory for temperatures which reach 538° C intermittently. The problems encountered are allied to, but somewhat different from, those in the manufacture of corrugated paperboard.

In some types a flat sheet is spotted or entirely coated with sodium silicate, either $\text{Na}_2\text{O}, 2.9\text{SiO}_2$ or $\text{Na}_2\text{O}, 3.3\text{SiO}_2$, and wound into a large roll with a crimped sheet thus holding the flute tips in place until the bond is dry. In some cases the crimped sheet is stiffened and filled ("tempered") by first spraying or soaking with diluted silicate and then drying. Multilayer resilient pipes are built up by winding this single face sheet on a mandrel with adhesive applied to the flute tips as in the manufacture of paperboard ¹²⁷. When used, the half-rolls sawn from the mandrel product are bound with a sheet of cotton cloth and coated with $\text{Na}_2\text{O}, 3.3\text{SiO}_2$ solution at 41° Bé as the adhesive. In summer a higher gravity may be needed to keep the warm silicate from dripping.

Where a solid composition is formed by sticking individual fibers to form a sheet or a coating, $\text{Na}_2\text{O}, 3.75\text{SiO}_2$ solution may be preferred as it will dry out more completely and rapidly at a lower temperature and will react less readily. Such impregnation with more alkaline solutions is likely to lead to "blooming", (the formation of Na_2CO_3 hydrate on the surface after aging).

Where a solid board or coating is produced by impregnation of paper

or by building up with fibers a more dilute adhesive solution is required.

Solid sheets are used for insulation against sound, fire, oil, and electric arcs. The sheets themselves may be bound to galvanized and metal surfaces with sodium silicate compositions ^{128, 129}.

Asbestos sheets are quite porous and white when dried. In order to avoid discoloration by reaction with the silicate adhesive the viscosity of the latter must be controlled to reduce wetting. There is some reaction between the mineral and sodium silicates particularly at temperatures of 100° C and higher and insoluble silicate which is described as "hard and semi-crystalline" may be formed ¹³⁰.

Methods of increasing the water resistance are similar to those already mentioned, more or less complete reaction with calcium compounds and the addition of ZnO or alum to the adhesive composition ^{129, 131}.

Resistance to weather is readily obtained by impregnating the cotton jacket with asphalt.

(c) *Mica*

The variety of properties exhibited by sodium silicate adhesives has long been used in forming sheets of mica such as are used for insulators. For ordinary use it is only necessary to press and set cold. The adhesive is sanitary and there is no added fire risk. The necessary flexibility may be obtained by control of moisture content while for use at higher temperatures, the pressed sheet may be cured at conditions of increased temperature and pressure ¹³⁰. This will bring about some chemical reaction resulting in increased water resistance and a corresponding increase in the apparent $\text{SiO}_2:\text{Na}_2\text{O}$ ratio and therefore the more alkaline Na_2O , 2.4 SiO_2 solution is recommended ¹³².

Dehydration increases the electrical resistance of such insulators. If at the same time the adhesive is kept away from exposed surfaces, the resistance is even better.

The slow rearrangement of micelles when solutions of differing ratio are mixed can bring about increased usefulness. The silicate of a lower ratio appears to have better working properties while higher ones give better final properties to the bond ¹²⁹ (see § 16 a).

The use as a binder for similar materials such as vermiculite, zonolite, kieselguhr, slate, etc. has been described ¹³³⁻¹³⁶.

(d) *Mineral Wool*

Mineral wool is held in position in the bat by dilute (20° Bé) adhesive solutions applied as a spray either to layers of the fibers or as they fall into

place. The proper dilution depends on the rate at which the spray loses water. Where resistance to water is important, more silicious ratios are used and oil may be added to the fiber mass to actually repel the water. Some fibers themselves have a low resistance to attack and in such cases, more alkaline adhesives are just as satisfactory^{137, 138, 139}.

§ 16. HETEROGENOUS MIXTURES

(a) *Calcium carbonate*

Adhesive mixtures of sodium silicate and calcium carbonate in the form of whiting, limestone or dolomite, etc. have long been known¹. CARTER¹⁴⁰ was the first to find that water resistant adhesives could be formed if the sodium silicate were more alkaline than the common commercial "neutral" silicate $1\text{Na}_2\text{O}, 3.3\text{SiO}_2$. A mixture of 25 parts Na_2O , 2 SiO_2 at 60° Bé, 25 parts water and 60 parts of whiting gave a substantially insoluble bond on paper board after about a week of cure. This bond may not be strong enough for plywood.

Subsequent study² has shown that alkaline and silicious silicates differ widely in their behavior with calcium carbonates. The alkaline silicates act very much more rapidly with a sharp upturn in viscosity after an initial period of slow reaction. They may show an enormous deceleration of the rotor during a measurement of Stormer viscosity, indicating dilatancy. The more silicious silicates have a much longer period of slow reaction and the rise in viscosity when it occurs is very much less. Such mixtures show an enormous acceleration of the rotor during measurements, indicating thixotropy. A precipitated chalk or a natural calcium carbonate crystallized as aragonite is likely to be reactive but calcite crystals react little if at all. The reaction which occurs forms an isotropic material on the surface of the particle. A great deal more SiO_2 is insolubilized when an alkaline silicate having a ratio 2.0 SiO_2 : 1 Na_2O or less is used than when the more silicious silicates are employed. There is a quantitative relationship between the temperature and the induction period and the temperature coefficient averages about 4 over a wide range of silicate ratios. A mixture which barely shows evidence of action at 20° will set very rapidly at 40°. The effect of increasing the concentration of the silicate solution seems to be directly related to the silica content and reaction is also increased by the use of more finely divided calcium carbonate.

Although a sodium silicate adhesive may not be satisfactory for gluing northern hard woods such as birch and maple the addition of about 25

pounds of a lime-free finely ground whiting to 100 pounds of "neutral" ($\text{Na}_2\text{O}, 3.3 \text{ SiO}_2$) silicate solution gives a satisfactory strength and the panels may be sawn in about 3 hours. Dolomite, alkaline earth carbonates or mixtures of them may be added to give a more permanent bond for wood, wallboard, or roofing granules ¹⁴¹.

Use of mixtures of silicate solutions has also been found useful. Equal parts of sodium and potassium silicates in a composition with calcium carbonate are recommended by FRANKE ¹⁴² for wallboard and WARE ⁸ suggests mixing $\text{Na}_2\text{O}, 1.65 \text{ SiO}_2$ with $\text{Na}_2\text{O}, 3.3 \text{ SiO}_2$ and calcium carbonate in water resistant adhesives for binding particles of grit to a backing material. The more alkaline silicate adds tenacity and reactivity while the more silicious acts as a thinner and reduces any hygroscopic tendency on the part of the alkaline ratio. One would expect that these mixtures should not be made up long before use.

(b) *Starch*

Silicate adhesives containing minor proportions of starch are not widely used. In general, they are quite compatible if an alkaline starch is used or if a sufficiently alkaline silicate is used when acid starches are incorporated. Dextrin is also readily incorporated.

THOMPSON ¹⁴³ advocates the dispersion of ungelatinized starches in soluble silicate adhesives used in laminating. Heat used to form the bond gelatinizes the starch and gives a quick initial bond.

The starch is also said to help in retention of water in the aged bond and to reduce the adherence of the adhesive to hot metal plates.

Silicates are included in starch dispersions to provide stiffness and bond strength, improve the wetting action of the adhesive, the keeping quality, or the consistency. A little silicate is sometimes added to a starch adhesive when a very hard sheet is to be pasted ¹⁴⁴. The silicate may be relied on as a source of alkali for controlled partial hydrolysis of starch ^{145, 146, 147}.

An adhesive having equal weights of liquid silicate and starch is used for bonds to metal surfaces and somewhat similar mixtures have been used to form balsam wool and rock sponge ^{3, 139, 148}.

(c) *Protein*

Many proteinaceous materials have been used as adhesives and sodium silicate has often formed part of the composition. In some cases it has

served to modify the working properties and in others to provide a buffered alkali. Again the silica micelle is used to insolubilize other components or to react generally in a colloidal sense with the protein molecules. Each mixture will differ in properties and use depending on the type of protein and the sodium silicate ratio.

Some of the properties which should be considered when dealing with mixtures with sodium silicate are outlined as follows: Proteins are molecules of colloidal size. Many are considered as convoluted, highly polar and having chemically reactive groups. Natural rubber particles are said⁹ to owe their negative charge to proteins absorbed on the surface. Glycinin is the principal form of protein found in oil seed flours. It is similar in some respects to casein derived from milk. Both are globulins. One of the important differences is that glycinin does not coagulate when the solution is boiled. The globulins themselves differ considerably from the albumins such as blood albumin in that they are absorbed preferentially to albumin on negatively charged particles as a mono-layer whereas the albumins do not unroll and are absorbed as globular molecules. Albumin on the other hand is absorbed preferentially to glycinin on positively charged materials. The salt concentration plays an important role. Albumins are soluble in distilled water whereas the globulins are insoluble at a pH near the neutral point¹⁴⁹. It is evident that sodium silicate as an alkaline salt solution containing negatively charged silica micelles will act specifically with the proteins according to their charge and reactive groups. It would be expected that both condensation and hydrogen bond formation might occur*.

Because of the similarities between the proteins the formulae first used for adhesive compositions were quite similar but with further study specialized mixtures have been prepared to obtain the best results from each material. Perhaps the best description of the preparation and conditions of use of vegetable proteins is given by BURNETT and PARKER¹⁵⁰. They show that with the proper formulation vegetable protein adhesives can meet the specifications for casein glues used on wood. Sodium silicates are used to improve the spreading qualities, promote penetration and thin the adhesive. Such mixtures are best used on soft woods such as the Douglas Fir of the northwestern United States but they are also largely used in the east and south for box shooks made from hard wood. Spreads varying from 35–40 pounds to 70–75 pounds per 1000 sq. ft. of glue line have been reported. Bonds are usually formed at about 150 pounds per sq. inch and 75° F. Burnett et al show that with proper formulation standard birch veneer can be made with a wet strength of 151 pounds per sq. inch

* Cf. Chap. 2.

after soaking while reports on $3/8''$ fir panels show that adhesives made with castor bean press cake may reach a strength of 175 pounds per sq. inch in tensile shear after soaking two days¹⁵¹.

More complex mixtures contain materials such as sodium chloride, zinc chloride, aldehydes, rubber, amines, paraffin and clay.

It has been generally believed that a highly caustic solution was needed to obtain water resistance with the vegetable proteins just as has been found to be the case with casein. The sodium silicates, if more silicious ratios were used, were added after a stronger alkali had had opportunity to react. Recent patents¹⁵² however, disclose the preparation of a vegetable protein adhesive containing silicious sodium silicate as the only alkali. It is satisfactory for use on high speed laminating machines and has a wet strength which is at least satisfactory for paper products.

Sodium silicate has been added to increase the strength and water resistance of blood albumen adhesives^{48, 153}. The early mixtures used silicates less alkaline than the $1\text{Na}_2\text{O}$, 2.0SiO_2 solutions. STERICKER and CLEVELAND found that by using more alkaline silicates they could form a water resistant bond from a dry powder by release of alkali in the bonding step instead of by heat treatment.

Fertilizer grades of blood albumen require more alkaline additives. The mixtures are used with hot presses in forming plywood. In these, lime and silicate are often allowed to react to free the caustic at the proper time. Vegetable seed flours also containing protein react with the same reagents and may be added to reduce the overall cost¹⁵⁴.

Casein adhesives containing sodium silicate, usually the more silicious ratios, have also been used for many years. The silicate has generally been considered as a means of extending the working life. The use of silicate of soda in place of the hydrolyzable salt in these mixes makes a desirable, less alkaline, cheap glue with good strength and water resistance. Because of the presence of colloidal silica the working properties are considerably different. Where lime was not added with the sodium silicate the glue was "softer" and increased the life of knives and saws^{48, 155}.

More recently there have been a number of patents covering mixtures of casein with vegetable protein flours such as soya, peanut, cotton seed and castor bean. The vegetable protein has generally been added to reduce the cost without seriously affecting the water resistant properties.

(d) *Rubber Latex*

Rubber latex particles have a negative charge and are lyophobic. They

absorb negative ions from solution with an increase in negative charge. The negatively charged colloidal sodium silicates if added slowly may be mixed readily with rubber latex dispersions over a wide range. A thickening occurs and a homogeneous product can be obtained varying in consistency from a watery fluid to a non-flowing paste. The sodium silicate increases the tack of the mixture and provides better working properties¹⁵⁶. The rubber content provides flexibility and water resistance depending on the proportions of the two materials. Silicate improves the wetting and setting properties and in the proper formulation gives maximum bond strength and increased stability. More care in formulation is usually required for synthetic latices than for the natural latex^{157, 158, 159}.

NAZZARO¹⁶⁰ lists the salt stability of latices in terms of the amount required for coagulation. He found that 0.83 moles of a Na_2O , 3.3 SiO_2 solution of specific gravity 40° Bé was the limiting quantity. This compared with 0.21 moles of NaCl and 2.23 moles of benzoic acid. Other salts were much stronger coagulating agents and require only 0.1 to 0.01 of these concentrations.

Special compositions are used for shoe soles and trim, foxing on tennis shoes, layers of fabric and wood for shoe soles, trimming material for sheeting, gauze bandages. Other compositions form adhesives with controlled strength and resistance to shock^{119, 161}. JONES¹⁶² found that fibrous materials could be bound to aluminum with such mixtures if the aluminum were first coated with aluminum silicate by treating with sodium metasilicate solution. Others have sand blasted steel before applying the adhesive composition as a coat which could be bonded to rubber with plain latex adhesives. Jones found that a silicate ratio more alkaline than $\text{Na}_2\text{O} : 3 \text{SiO}_2$ tended to cause creaming while a much more silicious silicate reduced the adhesion.

The best formulation of silicate and latex for any particular use depends on the permissible alkalinity and water loss as well as the strength and water resistance and permanence required. The optimum must be determined by trial. The shear strength in a cold set birch veneer joint as the proportion of a natural latex and dilute $1\text{Na}_2\text{O}, 2 \text{SiO}_2$ solution was varied in one series passed through a maximum. A high resistance in shear was found but a rather low strength in tension. Such characteristics are required in palletizing adhesives¹¹⁷.

Sodium silicate has been mixed with dispersions of rubber to form adhesives for many years. These compositions are usually boiled with one or more of the components of the complex in order to stabilize the dispersion¹⁶³.

(e) *Miscellaneous*

Silicates have been used with a great variety of materials some of which react chemically and some by surface activity. Others are either fillers or may be mixed without noticeable reaction.

Various organic compounds such as coumarone indene resin¹⁶⁴, phenolic resins¹⁶⁵, viscose¹⁶⁶ have been used. Other forms of protein such as collagen¹⁶⁷, gelatin¹⁶⁸ and Irish moss, crude algin¹⁶⁹ have been mentioned.

On leather a sodium silicate having a ratio of $1\text{Na}_2\text{O} : 3.3 \text{SiO}_2$ at 42° Bé has been found useful. The silicate may be diluted and mixed with 1.2% of clay as a filler. Carboxymethylcellulose, otherwise known as sodium cellulose glycollic acid or Tylose HBR or Zell-leim has been found to be miscible with sodium silicates over considerable ranges of ratio and concentration.

SARASON¹⁷⁰ claimed that the addition of traces of an extract of licorice (glycyrrhizen) greatly enhanced the silicate bond strength.

Inorganic compounds which do not ordinarily react with sodium silicate such as the phosphates^{38, 39}, borax³⁷, metal ammines¹⁷¹ have been mentioned as well as other compounds which will form precipitates, such as zinc oxide¹⁷² and copper sulfate¹⁷³ the latter of which was used in a starch adhesive.

Insoluble fillers such as aluminum fluoride and flint have formed water resistant adhesives¹⁷⁴. Others have added talc²⁶ and asbestos⁴⁹. JOHNSTON¹⁷⁵ used a mixture with Portland cement, sodium metaphosphate and sodium fluoride to bind asbestos or asphalt-impregnated fabric layers with a water and fire resistant bond.

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B. INORGANIC CEMENTS

§ 1. INTRODUCTION

This section on cements is planned to direct the reader to sources of fuller information and not as a complete survey of inorganic cements. For general surveys of recent developments the annual reports by PAYNE are useful¹⁷⁶. The standards supported by the American Society for Testing Materials and other groups have not been generally surveyed but contain much information useful for specific applications.

Those who need specific recommendations for general repair work or miscellaneous use will find recommended formulae compiled in technical journals¹⁷⁷⁻¹⁸¹.

§ 2. HYDRAULIC CEMENTS

Of the inorganic cements the most widely used are those known as hydraulic. Portland cement is that most generally recognized and volumes

are available on its properties^{182, 183}. There is little justification in this review for going further than to say that hydraulic cements set by crystallization and gelation of siliceous components and they require much water to form a good bond. The strength and water resistance of the bonded structures are influenced by additives among which are finely divided silica and sodium silicates. The latter must be present in a form which dissolves slowly^{184, 185}. Where solutions of alkali silicates are used the mass sets rapidly and is effective as a plug for leaking holes in containing walls.

The siliceous components of hydraulic cements are rather slow to react and full strength may not be obtained for weeks. The final product is susceptible to attack by both acids and alkalis and will not withstand temperatures above about 500° C. It is evidently not useful for many applications.

Other forms of the hydraulic cements are those with a high alumina content and those formed from trass and residues of volcanic action. Of similar nature are the cements which may be formed from blast furnace slag. PURDON¹⁸⁶ has made an extensive and interesting study of the effect of alkali and alkaline chemicals on slag compositions used as cements. The following range of slag compositions is narrower than some others reported but is representative.

SiO ₂	32.0–27.7%	CaO	48.2–39.6
Al ₂ O ₃	23.5–13.6%	MgO	4.5– 0.3
FeO	3.2– 0.5	SO ₃	2.3–trace
MnO	2.0– 0.1	S	1.9– 0.4

Blast furnace slag rapidly chilled and granulated is a vitreous product which will itself set slowly in the presence of water but it is usually used in mixtures with Portland cement or with lime or anhydrite. In the latter case 10–20% of anhydrite along with a small quantity of slack lime makes what is known as “ciment sursulfate”. PURDON found that a “relatively small quantity of an alkali is a much more efficient accelerator. The resulting cement has greater strength both initial and final than Portland (Table 40). The optimum quantity of caustic soda is 5–8% of the mixing water cements made in this way apart from their characteristically high early strength have the following advantages over Portland: (a) heat of hydration extremely low, (b) concrete is practically water tight, (c) low solubility in pure or aggressive waters” (Fig. 128). However, the alkalis could not be incorporated in the slag mixture and the proportion of

alkali depends on the quantity of water rather than that of the slag.

PURDON concluded that the alkali acted merely as a catalytic agent in making possible a more rapid crystallization from the glassy slag condition. "This hypothesis is strengthened by the fact that it is possible to recover

from a set slag mortar, by washing, almost all the alkali used as activating agent, without appreciable dissolution or carrying down of other substances".

He has found too that iron bars used as reinforcement in activated slag concrete exposed to moist air for 5 years showed no signs of attack in spite of the general supposition that the sulfide would increase corrosion.

LADWIG's¹⁸⁷ work on the development of water resistant Trass cements and mortars of high elasticity by admixture

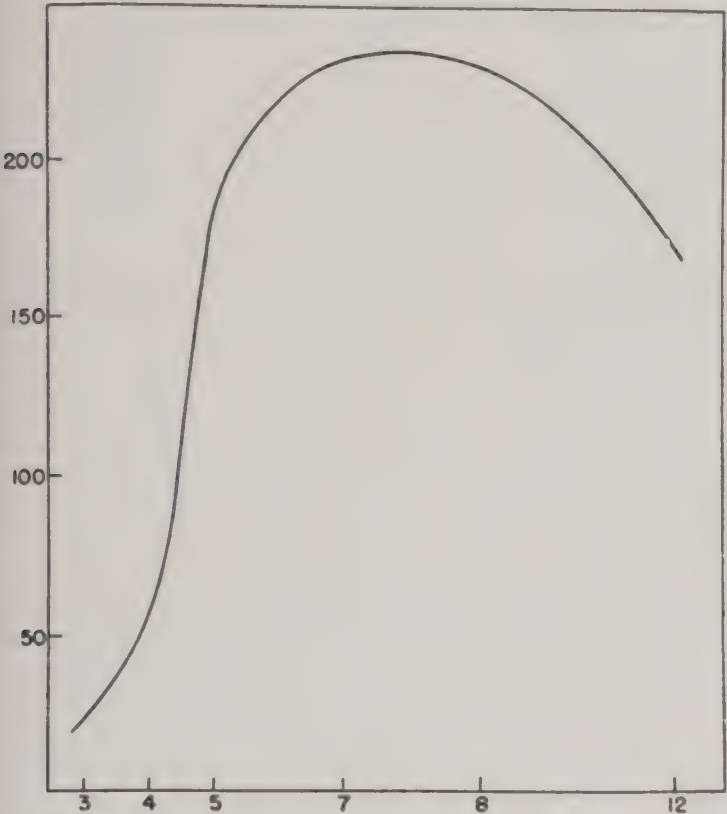


Fig. 128. The crushing strength of a concrete made with slag cement reached a maximum strength after 24 hours at about 7% NaOH and a pH of 14.1. Abscissa, NaOH in mixing water (%); ordinate, crushing strength (kg per s.q. cm.). (PURDON).

TABLE 40

CRUSHING STRENGTH (in lbs/sq. in.) OF SLAG CONCRETE ACTIVATED IN SIX DIFFERENT WAYS AND COMPARED TO A NORMAL PORTLAND CEMENT (PURDON)

Concrete	1 NaOH 6% soln.	2 Na ₂ CO ₃ + Ca(OH) ₂	3 Slaked Lime 20%	4 Normal Portland 41.4%	5 White Cement 41.4%	6 Anhydrite 18% slaked lime 2%	7 Normal Portland as Standard
Crushing Strength:							
24 hours	3555	4750	1052	1223	640	1546	2522
3 days	4806	6001	3214	3484	2218	3953	3839
7 days	5532	7153	5347	5660	3072	4422	4906
28 days	7295	7693	5816	6952	5247	5794	6832

References p. 383

TABLE 40 (Continued)

CRUSHING STRENGTH OF SLAG CONCRETE (in lbs/sq. in.) CURED IN ARTIFICIAL SEA WATER (PURDON)

Accelerator: $\text{Ca}(\text{OH})_2 +$ (small quantities)	2NaCl	Na_2SO_4	$\text{NaCl} +$ $\frac{1}{2} \text{Na}_2\text{SO}_4$
24 hours	1024	1351	1067
2 days	1602	2602	2147
3 days	2233	3498	2929
7 days	4180	4948	4920
28 days	5844	7380	5318
3 months	8021	8930	7650
year	8760	9783	9414

with vitreous sodium silicates suggests that they should have been included in a study of alkalies on slag cements.

§ 3. PLASTER OF PARIS

Another widely known cement is plaster of Paris made from gypsum¹⁸⁸⁻¹⁹⁰. A partially dehydrated gypsum, $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$, is quite soluble in water at low temperatures and rapidly recrystallizes to the dihydrate, gypsum, forming a hard mass when dry. The solubility of the gypsum itself though low by usual standards makes this cement inapplicable under conditions of high humidity or exposure to water but it may be impregnated

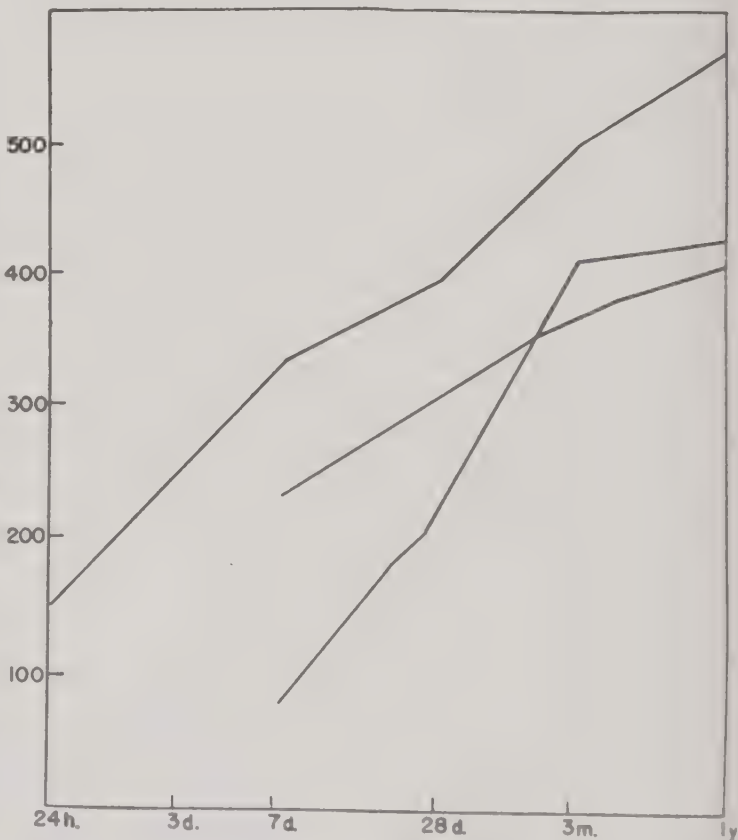


Fig. 129. The final strength of the optimum 72.3% slag-27.7% Portland cement was greater than that of pure Portland although a 100% slag cement was stronger at all times. Normal 1: 3 mortar was used. Abscissa, Time (24 hours to 1 year, log. scale); ordinate, crushing strength (kg. per sq. cm.) (PURDON)

with resins. It is also used where a gas-proof cement is required, and such mixtures usually contain fibrous material or sand. Asbestos reacts in the presence of moisture to form crystalline growths of magnesium sulfate, similar to the efflorescence caused by reaction of carbon dioxide with more alkaline cements.

A use instructive of its properties is in the preparation of molds or investments used to reproduce wax designs as for instance in the preparation of dental inlays. The gypsum itself when forming by recrystallization expands but the mold shrinks again when calcined to remove the wax and water. This expansion and contraction is controlled by the inclusion of cristobalite. The thermal expansion of cristobalite on drying is greater than that of quartz and mixtures with Plaster of Paris show a nearly constant amount of expansion over a considerable range of temperature. The composition can be adjusted to allow for the shrinkage of an alloy such as a gold alloy. Other necessary characteristics are rapid set and a smooth surface which will reproduce minute details.

Because of the accuracy with which the thickening time can be controlled and full strength is obtained soon after setting, Plaster of Paris is used in oil well bore holes to shut off water, to "kill" gas wells, for shot-tamping, and to recover lost circulation in cavernous limestone¹⁹¹.

Ordinary plaster of Paris is formed by heating gypsum to about 120° C thus boiling off the excess water down to about the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ composition. The product is further dried at about 150° C and forms a porous mass which is ground into a powder. A more recent type of plaster of Paris is that known as "Hydrocal" which is prepared by heating gypsum at 17 lbs/sq. in. of steam (123° C) for several hours. This results in the formation of finely divided separate and non-porous crystals of the $\frac{1}{2}$ hydrate composition which require much less water to make up the plaster.

TABLE 41

THE EFFECT OF THE RATIO OF WATER TO PLASTER ON THE PROPERTIES OF PLASTER OF PARIS USING A MIXING TIME OF 1 MINUTE (SKINNER)

Water: plaster ratio in cc/gram	setting time minutes	setting expansion %	dry crushing strength lbs/sq. inch
0.45	3½	0.51	3800
0.60	7½	0.29	2600
0.80	10½	0.24	1600

The strength of the plaster of Paris is increased by drying. After 2 hours and a loss in weight of 5.1% the crushing strength was 1400 lbs/sq. in.

After a loss of 17.4% at 8 hours drying time the strength was 1700 whereas the crushing strength reached a maximum of 3400 lbs/sq. in. after a loss of 18% in about 24 hours.

Because the Hydrocal mixture sets with much less moisture it forms a much harder mass or "stone". Crushing strengths may approach those of Portland cement although it will give an initial set in 15–20 minutes. A representative formula is

Hydrocal 95 – 98.4%
 Rochelle salts 1 – 5%
 Retarder 0.1%
 Pigment 0.5 %

Retarders used may be borax, sodium citrate or similar materials. The Rochelle salt is an accelerator. Other accelerators are sodium or potassium sulfate and sodium chloride. This formula yielded a cement with a dry crush strength of 7500 lbs/sq. in. when suitably prepared¹⁹².

A mixture of plaster of Paris and Portland cement known as Spence's plaster contains alum and sand. It has a low expansion on setting and a high dry crushing strength.

Keene's Cement is a combination of gypsum burned with aluminum sulfate or borax.

§ 4. LIME MORTARS

These are also widely known in the construction industry. They set by hydration and crystallization of CaO and MgO components which give rise to the designations "high lime" and "high magnesia". The ASTM standards for 1946 give the following limiting compositions¹⁹³.

	Calcium lime	Magnesium lime
CaO (min. %)	75	—
MgO	—	20
CaO + MgO (min. %)	95	95
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ (Max %)	5	5
CO ₂ (Max %)	10	10

The calcined limestone is "slaked" with water to a smooth workable paste with sand and fibrous materials to lessen contraction and cracking on drying.

Most lime now in use is carefully hydrated Ca(OH)₂ with all lumps carefully removed. This results in more reproducible mortars as it pre-

vents localized overheating which may result from uneven hydration.

The crystallized lime hydrate gradually carbonates on exposure to air and increases in strength thereby¹⁹⁴.

§ 5. SOREL CEMENT

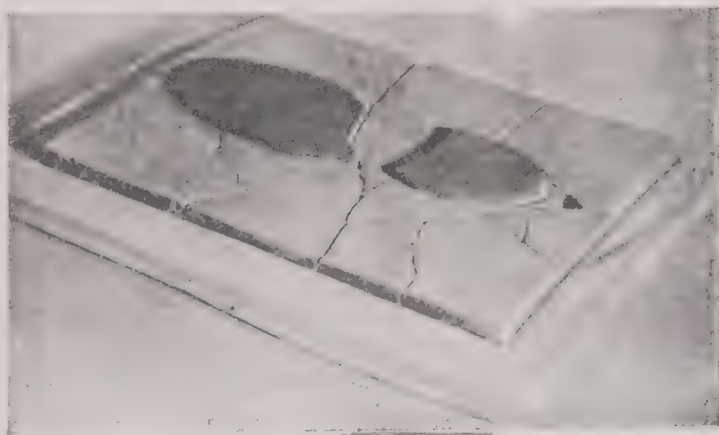
Magnesium chloride cements described by Sorel in 1876 are similar to the dental cement zinc oxychloride and have been capably reviewed by HUBBELL^{195a}.

These cements, originally widely used for floors and wall plaster were found to be too soluble to withstand weathering or washing. They had a large coefficient of thermal expansion dependent on critical factors of composition and preparation which were difficult if not impossible to control. However, they are three or four times as strong as Portland cement, set rapidly, are resilient, and they bond readily to many materials. Adhesion to sand blasted glass exceeded 100 pounds per sq. inch. HUBBELL studied the effect of changes in composition and found that the addition of copper powder overcame the



Courtesy of Mellon Institute of Industrial Research

Fig. 130. The cylinder of Sorel cement on the left contained 5% copper and held water for two weeks without the disintegration shown in the cylinder on the right prepared without copper.



Courtesy of Mellon Institute of Industrial Research

Fig. 131. The footprint of Sorel cement with 10% copper resisted a water spray for three months. The surrounding Sorel cement washed away to a depth of $\frac{1}{4}$ inch.

major drawbacks to use of such cements. (Fig. 130 and 131). The copper forms insoluble blue-green $3\text{CuO} \cdot \text{CuCl}_2 \cdot 3\text{H}_2\text{O}$ by reaction with the magnesium chloride used to react with magnesium oxide in the formation of magnesium oxychloride gel, $(\text{MgCl}_2 \cdot 3\text{Mg}(\text{OH})_2 \cdot 8\text{H}_2\text{O})$, Sorel's cement.

"Perhaps the uses that take fullest advantage of the chemical properties

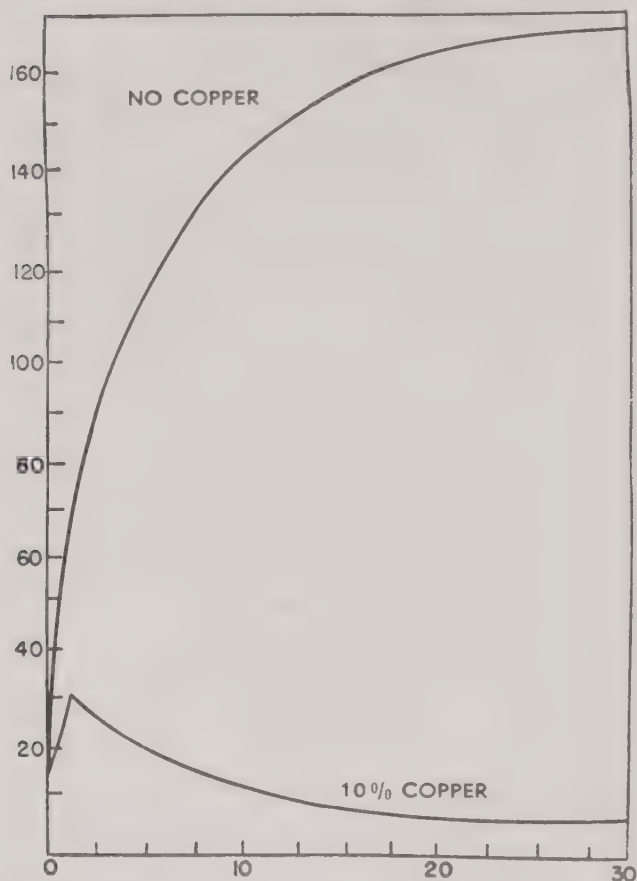


Fig. 132. The addition of ten percent copper to unsound Sorel cement containing some lime entirely prevented the expansion which caused disintegration in one month. Abscissa, age in days; ordinate, expansion ($10^{-3}\%$ of bar length) (HUBBELL).

of these cements are those in kitchen and hospital operating room floors. In the former the cement's resistance to damage by cooking fats and greases is important, and its chemical nature due to the copper compounds it contains prevents the growth of mold and most bacteria on the surface. This is important to sanitation and prevents the development of odors from spoilage of food waste on the floor. It is probably also responsible for the cockroach repellence of the floor."

"In the case of hospital operating rooms these benefits to sanitation are, of course, important and, in addition, the floor must be capable of conducting away static electricity in order to prevent ignition of

anaesthetic gases used in the room. These cements lie in the range specified by the National Fire Protection Association (25,000 ohms–500,000 ohms)"¹⁹⁶

The optimum proportion of Cu is about 8 to 10%. Such a product "is highly insoluble in water and free from excessive expansion even when placed in contact with materials that contain lime or when magnesium oxides are used that would otherwise have caused disastrous increases in volume, it is almost entirely free from efflorescence, and has a strength when dry nearly twice and when wet nearly three times that of the

TABLE 42

EFFECT OF THE CONCENTRATION OF THE $MgCl_2$ SOLUTION ON THE PROPERTIES OF SOREL CEMENT (HUBBELL)

Concentration of gaging solution °Bé	Tensile Strength dry — 30 days lbs/sq. in.	Linear change percent of length stored at 70% R.H.		
		1 day	10 days	90 days
18	1053	−0.030	−0.078	−0.044
22	1152	0.003	−0.009	−0.014
26	1272	0.036	−0.020	−0.009
30	897	0.037	0.048	0.045
36	462	0.007	0.012	0.006

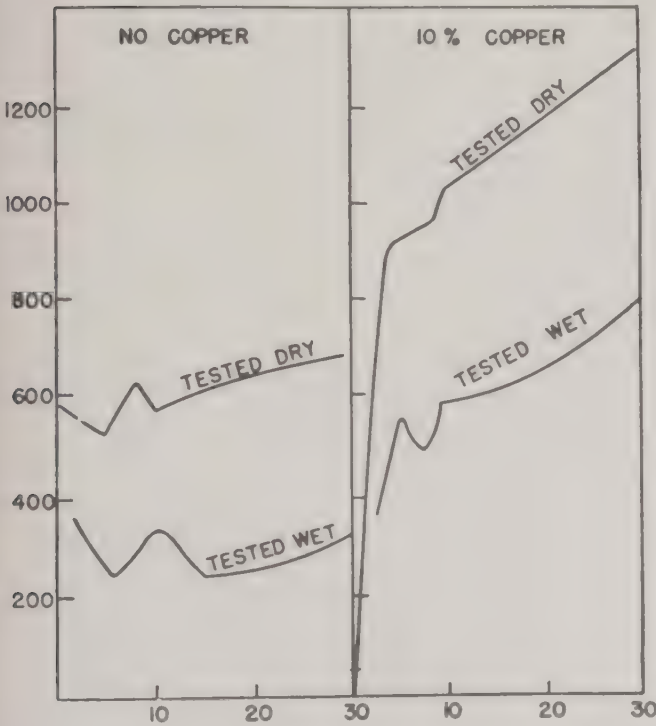


Fig. 133. The wet and dry tensile strengths of Sorel cements containing ten percent copper are greater and rise more rapidly than those without. (15% plastic Magnesia, 85% aggregate, 24° Bé $MgCl_2$ solution to standard consistency). Abscissa, age in days; ordinate, tensile strength (lbs/sq.in.). (HUBBELL).

original cement” (Figs. 132–134). About 17–18% by weight of plastic magnesia, 10% Cu powder, 72% aggregate and 22° Bé $MgCl_2$ solution in the ratio of 6 : 1 : : MgO : $MgCl_2$ is recommended.

The cost and high heat of reaction prevent use of these cements in large masses. The addition of fine fillers helps to avoid cracking.

BENNET¹⁹⁷ lists one adhesive composition as formed from the following two mixtures:

- (1) MgO 40
 $BaSO_4$ 40
chalk 20
- (2) $MgCl_2$ (27° Bé) 60
 HCl (21° Bé) 20
 H_2SO_4 (22° Bé) 20

It is proof against water and hydrocarbons and forms a hard durable cold-setting cement for use as flooring and stucco. In the latter use it should be faced with crushed stone to give resistance to weathering.

Cements of somewhat similar constitution have been found useful as

binders for refractory bricks of periclase. Electrically fused magnesia containing 2.5 to 5% of calcined sea-water magnesia wetted with a 24° Bé magnesium chloride solution gave the best results in a series of tests using other organic and inorganic binders fired at 1800° C¹⁹⁸ (Fig. 135).

Magnesia shapes fired to 1450° C gave satisfactory service in a furnace at 2000° to 2200° C under oxidizing conditions (Table 43).

Similar compositions have been used instead of sodium silicate to bind colors to roofing granules without the high degree of heat treatment usually required. Mixtures of pigment, calcined magnesite or magnesia, and 22° Bé $MgCl_2$ solution are thoroughly mixed and heated to about 40–50° to hasten the reaction¹⁹⁹.

Finely divided SiO_2 , 20% based on weight of MgO , improves the strength, volume stability and moisture resistance of Sorel cement²⁰⁰.

The efficacy of Sorel cement containing copper against cockroaches and microorganisms has been described^{201, 202}.

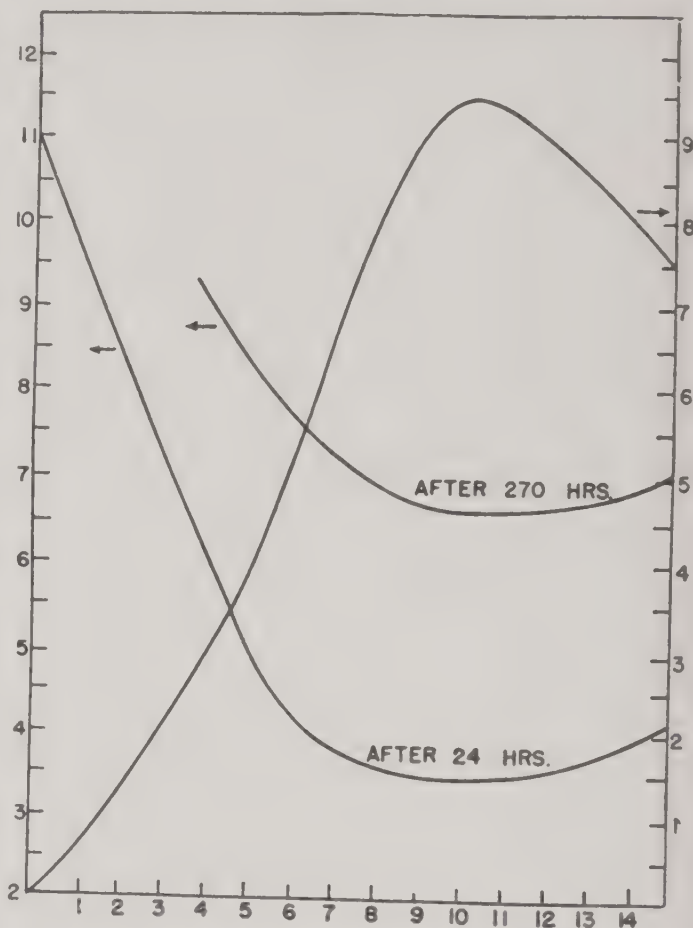


Fig. 134. Immersion in boiling water which was changed frequently completely disintegrated cement slabs aged 30 days in 270 hours unless copper powder was added. After this period the modulus of rupture was determined. Abscissa, Copper as % by weight; ordinates: left, weight lost in %; right, modulus of rupture (lb/in².) (HUBBELL).

§ 6. LITHARGE

Mixtures of glycerin and litharge either alone or with additives have been used for many years. One of the main uses is as a lining to protect cellulose digesters against acids; another use is as paint resistant to hydrocarbons.

TABLE 43
PROPERTIES OF PERICLASE REFRACTORY BRICKS BONDED WITH SOREL
TYPE CEMENT. (POLE, BEINLICH, GILBERT)

Body Composition	Bonding Agent 24 ⁵ Bé MgCl ₂	Initial set, hr.	Unfired Compressive Strength lb/sq. inch	Total Linear Shrinkage— 1800 C°, %
(A) 100% Periclase	11.00	6.5	1054	2.4
(B) 97.5% Periclase 2.5% sea water magnesia	12.5	7	3319	0.8
(C) 95% Periclase 5% Sea water magnesia	14.0	7.5	5572	1.7
(D) 90% Periclase 10% Sea water magnesia	15.5	6	6093	2.9

(C) and (D) developed hair line cracks on firing.

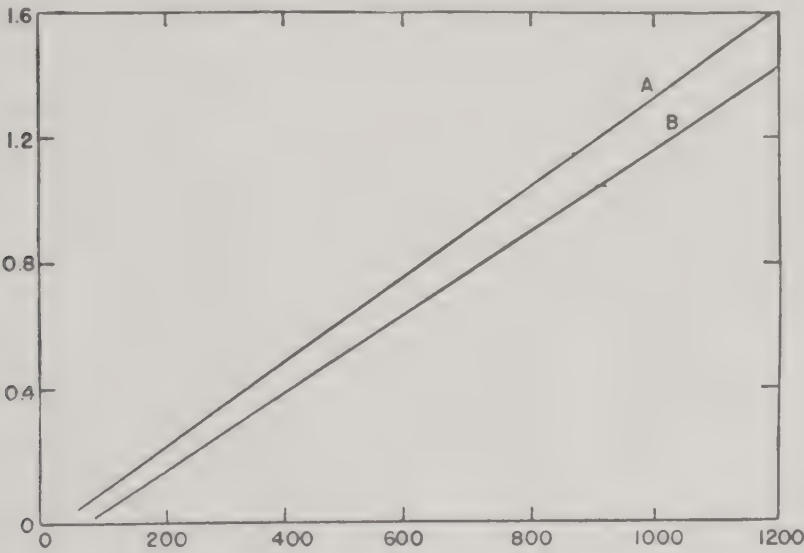


Fig. 135. The expansion characteristics of magnesia refractories, periclase and electrically fused MgO bound with MgCl₂ solutions are approximately the same (POLE, BEINLICH and GILBERT). Abscissa, temperature of specimen in °C; ordinate, expansion as % of length.

A — 97.5% Periclase — 2.5% sea water MgO
B — 97.5% electrically fused MgO — 2.5% sea water MgO.
Heating rate — 4° C per minute.

It is thought that this mixture of slightly diluted glycerin, 1 part, with lead oxide (PbO), 2 to 3 parts, which takes about one day to set forms a definite crystalline compound. The composition may be used on silica and various materials where resistance to weak acids and nitric acid is needed

but the cement does react with sulfuric acid. For ammonia gas conduits it is recommended to use 4–5 parts of PbO to 1 part of glycerin. This mixture should be ground to a putty and takes about two days to set.

A number of writers also recommend the addition of sodium silicate. Thus a mixture of 8 parts PbO , 4 parts Na_2O , 2.4 SiO_2 solution and 1 part glycerin will set in three minutes and be resistant to calcium bisulfate liquor. Some recommend a 1 : 1 mixture of sodium and potassium silicate solutions ^{203–204}.

Other more complex compositions have been suggested ²⁰⁵.

§ 7. IRON CEMENTS

Cements containing particles of iron and electrolytes such as ammonium and sodium chloride, vinegar, etc. appear to be increasing in use on radiators, iron covers and connecting lines. The main service is as fillers for unwanted open spaces. Setting appears to occur by corrosion of iron and crystallization of solids which provides adhesion between the adherend and the remaining iron particles. Such cements are not strong nor do they resist acids ²⁰⁶.

A simple formula for use with wrought iron is

iron filings	62%
NH_4Cl	1%
H_2O	37%

For attaching iron to stone either of the following formulae have been found safe and useful:

(a) sulfur	25%
iron filings	25%
silica	25%
vinegar	25%
(b) iron filings	24%
manganese dioxide	6%
gypsum	15%
rock salt	5%
Na_2O 3.3 SiO_2 solution (41° Bé)	50%

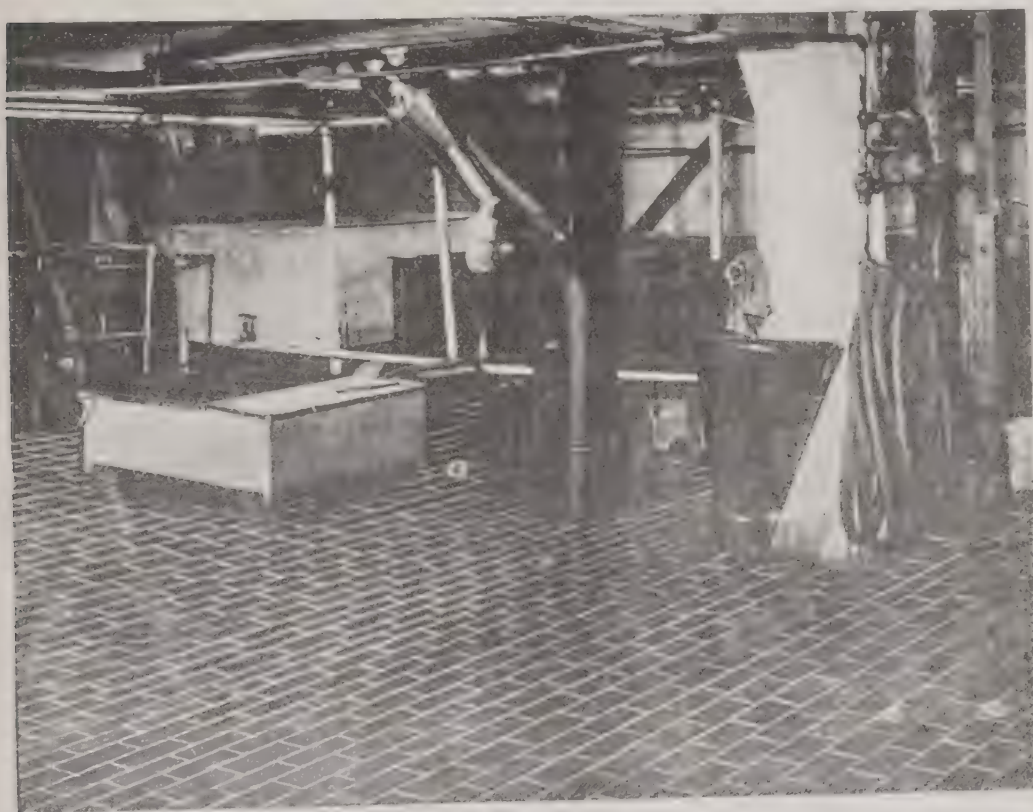
A dry powdered mixture contains

Aluminum powder	9%
Flaxseed meal	70%
Casein	12%
Sodium silicate	9%

In such a formula the silicate when dissolved for use will react with the protein of the meal and casein forming a gelatinous water resistant product. The silicate ratio should be more silicious than $\text{Na}_2\text{O}, 2\text{SiO}_2$ to avoid reaction with the aluminum powder.

§ 8. SULFUR CEMENTS

The sulfur cements ²⁰⁷ usually include some additives. Where there is none, resistance to shock, particularly thermal shocks is low. By the use of graded aggregate the normal 12% volume decrease, of sulfur may be reduced to



Courtesy of Atlas Mineral Products Company

Fig. 136. This floor set with a sulfur cement containing graded silica aggregate and a plasticizing agent has served a food plant for over a decade.

about 4%. These cements may be used only at relatively low temperature, that is, less than 93°C , because of the increase in coefficient of expansion when rhombic sulfur changes to the monoclinic form at 96°C . The melting point of the sulfur, 110°C , is also low. In preparing such cements it is necessary to keep in mind the equilibrium in melted sulfur between the

μ and λ forms. The μ form is found in greater proportion at higher temperatures (about 160°C) and crystallizes in a triangular pattern. Cements with this crystallization pattern have poor binding strength compared to those having the feathery crystals of the λ form more prevalent at lower temperatures, $130\text{--}140^{\circ}\text{C}$. Sulfur cements set up rapidly at low temperatures and have very high resistance to many chemicals. Improved physical properties may be obtained by incorporating very fine carbon black and polysulfides soluble in sulfur such as Thiokol (Fig. 136). The carbon black helps to release air, reduces voids and increases workability and tensile strength²⁰⁸. Silica now available in a similarly finely divided form should also be successful.

The general properties of elemental sulfur are tabulated by BACON and DAVIS²⁰⁹. In addition to those properties mentioned below the electrical conductivity is found to be the lowest of almost any solid, 1×10^{-17} reciprocal ohms per 1 cubic centimeter at 22°C compared to porcelain with 1×10^{-14} under the same conditions. It also has a very low heat conductivity as gram calories transmitted per second through a

plate 1 cm thick and 1 sq. cm in area at a temperature difference of 1°C over the range of $20\text{--}100^{\circ}\text{C}$: 6×10^{-4} may be compared to ice at 2×10^{-3} . The heat of fusion of the rhombic form is 14.9 gram calories per gram.

Fig. 137 shows the approximate solubility in many solvents. One formula reached a constant tensile value of 440 lbs/sq. inch when held in water for two years at 70°C . Sulfur cements are not broken down by water and they exhibit excellent resistance to inorganic acids. Their outstanding use is in tanks for holding solutions of mixed nitric and hydrofluoric acid at 72°C . Such liquids are used for pickling and cleaning aluminum and stainless

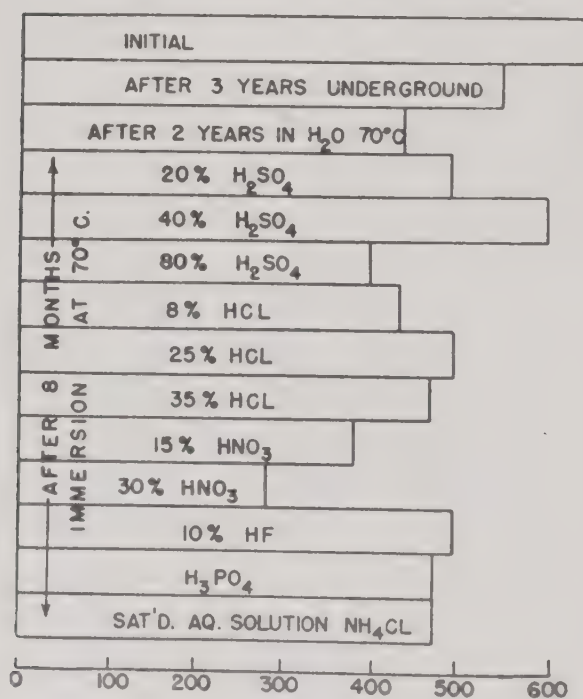


Fig. 137. Sulfur cements resist most non-oxidizing acidic materials even over long periods of exposure at temperatures below 90°C . Abscissa: tensile strength (p.s.i.) (PAYNE and DUECKER).

steel ²¹⁰. Organic acids are usually satisfactorily resisted except that oleic acid is destructive at higher temperatures. The sulfur cements show comparatively little resistance to strong bases or lime but will withstand intermittent use. Oxidizing agents such as chromic acid must be avoided. Vegetable oil and petroleum products are likely to be poor risks but most salts except calcium bisulfite are safe. They adhere well to metals in general but particularly well to copper. The strength of adhesion to terra cotta has been said to be 30–37 lbs. per sq. inch. Representative formulae for widely used commercial sulfur cements percent by weight are as follows:

	A	B	C	D	E
sulfur	58.5	59.5	58.8	99.5	58.8
ground silica	30.5	27.0	39.8		38.0
soapstone	10.0	10.0			
carbon black	1.0	3.0	1.0		2.0
olefine polysulfide		0.5	1.2		1.2

A comparison of the properties of these cements will be helpful in determining utility. (Table 44).

TABLE 44

A COMPARISON OF THE PROPERTIES OF REPRESENTATIVE SULFUR CEMENTS

	A	B	C	D	E
Coefficient of linear expansion in./°C (30°–93°) × 10 ^{–5}	3.6	3.8	4.3	7.7	4.5
Compressive strength lb/sq. in.	9781		6300		6159
Tensile strength lb/sq. in. *	880	707	650	250	830
Modulus of rupture lb/sq. in.	2194	2203	2052	1270	2377
Straming test	several long cracks	one	almost disintegrated		
Vol. shrinkage on setting – %	7.3		6.0		
Specific gravity	2.24		2.18	2.07	
Impact to break (relative)	0.37		0.26		
Porosity A.S.T.M. (% volume)			0.97		
Absorption A.S.T.M. (% water by weight)			0.52		
Thermal conductivity BTU/hr/sq.ft/°C/ft. (21° C)			0.25–0.29		

The strongest sulfur-sand mixture contains 40% sulfur and has a tensile strength of 400 lbs/sq. inch. This strength can be increased by using a finer

* Cf. 900 lbs. for a thin bond of sulfur on aluminum ²¹¹.

sand and a value of 650 pounds has been obtained. The modulus of rupture is 1558–2050 lbs/sq. inch and the coefficient of expansion is $6.3 \times 10^{-5} (^{\circ}\text{C})$.

MCKINNEY²¹² has published a useful paper on the testing of sulfur cements.

§ 9. COLLOIDAL SOLUTIONS

Some viscous inorganic solutions find a place in the cement art. Materials such as $\text{Al}_2(\text{SO}_4)_3$ which form gelatinous binders by reaction are used to some extent. On firing, the gel bond formed will lose the SO_3 component at about 770°C leaving alumina. The phosphates and borates are usually used in more complex mixtures.

Soluble silicate of soda is widely used in the formulation of cements and as such usually contains some filler. In general, the properties are those described for soluble silicate adhesives. On complete air drying the binder will retain on the average 15% of water. Baking at 100°C will leave about 6% but complete dehydration requires the use of high temperatures. Care must be taken to stay below the boiling point at all times in the drying cycle. Cements which set by reaction may require only air drying. Those which are designed to form a ceramic bond must be heated approximately to the liquidus temperature. This and the viscosity of the melt so formed will depend on the control of the reaction and the amount of dissolution undergone by the aggregate or filler. The presence of other salts will affect the viscosity and liquidus temperature of the glass.

In some cases, a pretreatment of clay with a sodium salt will remove, by base exchange, calcium or other ions which tend to destabilize a plastic mixture²¹³.

Many additives are such as to react directly with the alkali in the solution, for example sodium silico-fluoride, CaCO_3 , BaCO_3 , hydraulic cements, silicon, etc. Set is produced by formation of a crystalline or amorphous precipitate capable of maintaining a bond. Such mixtures are very widely used where exposed to corrosive conditions but no silicate can stand up against hydrofluoric acid or continued exposure to alkali.

The general literature on cements using soluble silicates has been surveyed recently and may be referred to for bibliography^{185, 214}.

There is fairly complete data available on the liquidus and viscosity of sodium and potassium silicate glasses and some information on numerous more complex systems^{215–216}.

Ground sand increases the body, reduces the moisture loss required for set and tends to increase the moisture resistance of the final cement by increasing the silica: alkali ratio of the soluble silicate. Increase in ratio

by reaction with sand, etc. appears most regularly where the cement is dried at elevated temperatures. Such cements are particularly adapted to high temperature use as they cannot be destroyed by heat and the liquidus temperatures can be made quite high. The overall softening point may also be increased by the proper choice of clay. WEBB is convinced that

TABLE 45

PROPERTIES OF REPRESENTATIVE ALKALI-SILICATES USED IN REFRACTORY CEMENTS (PHILADELPHIA QUARTZ COMPANY)

Alkali-Silica Ratio	Amt. of Silicate to make 100 lbs. solids	Liquidus * Temperature of solid silicate without filler	Order of fluxing effect on fillers
Na ₂ O : 3.75 SiO ₂	323	2012° F	1
" : 3.22 SiO ₂	266	1575 "	2
" : 3.22 SiO ₂	258	1755 "	2
" : 2.90 SiO ₂	233	1508 "	3
" : 2.40 SiO ₂	213	1525 "	3
" : 2.00 SiO ₂	185	1600 "	4
" : 1.60 SiO ₂	197	1550 "	5
" : 3.22 SiO ₂	121	1575 "	2
" : 3.30 SiO ₂	101	1575 "	2
" : 2.00 SiO ₂	121	1600 "	4
" : 2.00 SiO ₂	101	1600 "	4
K ₂ O : 3.91 SiO ₂	366	1405 "	1
" : 3.29 SiO ₂	254	1580 "	2

"The structure giving the greatest strength is hence not that in which glass is acting merely as a cement between the grains of filler, but in which the surface of the filler grains has been penetrated by interfusion, giving an interlocking structure with the glass" ²¹⁷.

POOLE ²¹⁸ has recently studied the effect of the presence of other cations on the viscosity of alkali silicate glasses in the softening range. He has found that the mixed alkali system (Na and K) does not exhibit additive properties so that a minimum in the viscosity relation is obtained but

	mol %
SiO ₂	60-70
Na ₂ O	10-15
CaO	0-20
Al ₂ O ₃	0-5

* Liquidus temperature is point at which silicate is completely fluid. Softening temperature is approximately $\frac{2}{3}$ liquidus temperature.

Fig. 138 for the systems included in $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ "additivity relationships are valid to a first approximation" within the limits: SiO_2 60–70, Na_2O 10–15, CaO 0–20 and Al_2O_3 0–5 mol. %.

As in Portland cements, silicious gels form important bonding agents. Most reactions between sodium silicate and acid materials or heavy metal oxides form gels or gelatinous precipitates. The strength of the final cement depends in large part on the water content of the solution at the time the gel forms. The lower the water content at the critical stage the stronger the bond tends to be.

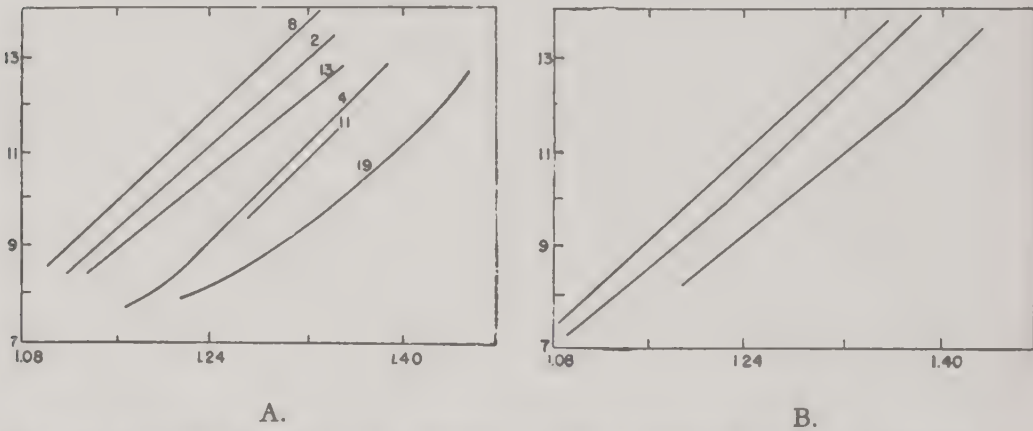


Fig. 138. Mixtures of sodium and potassium silicate glasses have a lower viscosity than either of the pure glasses. $\log n = a + b (10^3/\text{Ta})$. Abscissa, reciprocal absolute temperature ($10^3/\text{Ta}$); ordinate, viscosity on a logarithmic scale. (POOLE).

Batch No.	Na_2O %	K_2O %	SiO_2 %
Fig. A. 8	—	18.01	81.99
2	20.13	—	79.87
13	10.15	7.02	82.83
4	34.53	—	65.47
11	—	34.05	65.95
19	26.31	6.48	67.21
Fig. B. 9	—	24.50	75.50
3	24.82	—	75.18
16	12.91	11.34	75.76

Porosity of a silicate cement also depends on a number of factors. The modulus of elasticity is sometimes used as a rough relative index. If the cement is dried too rapidly puffiness may result bringing about a decrease in strength. Care must be exercised even up to 500°C as the last of the water content may be retained up to about that temperature. Soluble aggregates may also lead to increased porosity. It is well known that the proper grading of an aggregate is necessary to form a dense cement. If the

proportion of silicate solution is too little the aggregate may not be adequately wetted whereas if it is too great, a weak gelatinous bond may result in cements depending on reaction for their set. Where the silicate solution is too dilute the cement will be slow drying and again may form too weak a bond with the aggregate because gelation will tend to occur at a dilute stage or the adhesive will drain away from part of the surface.

Where acid and water resistance are required many of the same principles may be applied as have been mentioned in the section on adhesives. Inclusion of zinc oxide and calcium carbonates, etc. will tend to increase water resistance after sufficient time for reaction has elapsed.

The importance of the temperature of set and particle size of the additives is shown strikingly by work of the American Zinc Company ²¹⁹.

After one week at 90° C, hardened masses of ZnO powder and sodium silicates of varied ratio showed only the ZnO X-ray pattern. The hardest formed with Na₂O, 3.2 SiO₂ (42° Bé). After six hours at 500 lbs/sq. inch and 242° C, the most silicious and the most alkaline showed some reaction according to X-ray study and the hardest formed with Na₂O, 2.4 SiO₂ (52° Bé). This was the only mixture to show a reduction in weight lost on leaching although the Na₂O, 3.9 SiO₂ showed a change in X-ray pattern. After 900° C for 15 minutes, all showed definite crystal change. The least soluble products were made with the more silicious silicates.

In another series of experiments the relative consistency of mixtures using ZnO of uniform particle size was studied for three weeks.

Ave. Particle Size	5.0 μ	0.4 μ	0.16 μ	0.1 μ
2 hours 6 days 21 days	8 heavy very heavy	17 sticky taffy	480 taffy almost solid	too heavy solid solid

The fluosilicates set quickly and form cements of highly acid-resistant character and resistance to both acid and water is increased as the density of the cement is increased. Cements in which the pores are filled with silica are most resistant. However, such cements depending on some reaction with the silicate tend to have a lower strength than carefully dried silicate-sand mixtures.

VAIL ¹ gives the following figures for the tensile strength of briquettes formed from quartz, sand, and Na₂O, 3.3 SiO₂ of specific gravity 1.39.

Parts of Silica	Parts of Silicate	Tensile Strength of Briquettes dried to Constant Weight at 49° C
100	33.1	612
	31.3	556
	29.5	706
	27.8	1472
	26.0	1603

A study of binders used for periclase (MgO) refractories showed that Na_2O , 3.2 SiO_2 solution gave better results than any of the other commonly used materials fired to 1800° C¹⁹⁵.

TABLE 46

PROPERTIES OF MGO REFRACTORIES FORMED WITH COMMON BINDERS.
(POLE, BEINLICH AND GILBERT)

Binder	Specific Gravity of Agent	Weight Percent of added Agent	Initial Set (hr)	Unfired Compressive strength lb/sq.inch	Total Linear Shrinkage %
50% Na_2O , 3.2 SiO_2	1.20	11.75	0.5	492	3.3
25% Na_2O , 2 SiO_2	1.11	11.75	1	541	2.7
silica sol *	1.81	12.00	2.5	97	4.4
1% Dextrin	as solid	11.00	8	189	2.7
1% Flour	as solid	8.50	2.5	88	2.9
Molasses	1.22	10.5	1	— **	2.3

Fundamental studies of the characteristics of refractories of pyrophyllite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) have been made by GREAVES-WALKER *et al.*²²⁰. While most of their work on drypressed brick was done with sodium silicate binders, they have compared the effect of sodium aluminate, alumino-silicate gels and zinc phosphate besides certain organic binders. For overall results they prefer 1.5% (anhydrous basis) Na_2O , 3.2 SiO_2 solution (1.4 specific gravity). The addition of binder decreases porosity and shrinkage and decreases the pyrometric cone equivalent but increases the tensile, shear and compressive strengths.

* Na_2O : 40 SiO_2 with $(\text{NH}_4)_2\text{CO}_3$ to accelerate set.

** merely compressed and still plastic.

TABLE 47 a

PROPERTIES OF PYROPHYLLITE REFRACTORIES BOUND WITH COMMON MATERIALS
(GREAVES-WALKER *et al.*)

Binder Percent Anhydrous Basis	Percent	Dried Properties		Fired (Properties (1335° C)	
		Compressive Strength lbs/sq. inch	Apparent Porosity Percent	Apparent Porosity Percent	Linear Firing Expan- sion Percent
Na ₂ O :3.2SiO ₂ water					
0.00	4.5	2,200	13.50	19.45	2.0
0.40	3.4	2,610	13.79	17.00	2.0
0.80	2.8	2,705	13.84	17.15	2.0
1.20	2.1	3,315	12.76	16.20	2.0
1.60	1.5	3,731	12.51	15.95	2.0
2.00	0.9	4,680	12.15	15.50	2.0
NaAlO ₂					
0.00		2,200	13.50	17.45	2.00
0.45		2,520	14.02	16.25	2.00
0.85		2,915	13.06	15.15	1.90
1.20		3,680	12.58	14.95	1.90
1.60		4,540	12.29	14.55	1.80
2.00		5,405	11.67	14.10	1.90
2.40		5,610	11.60	13.15	1.90
Na ₂ O,Al ₂ O ₃ ,2.7SiO ₂ (gel) Sod. silicate					
0.0	0.00	2,200	13.50	17.45	2.00
0.2	0.15	2,180	13.09	16.05	1.99
0.4	0.30	2,613	13.02	15.65	1.99
0.6	0.45	2,908	13.01	15.15	1.99
0.8	0.60	3,000	12.71	15.10	1.99
1.0	0.75	3,175	12.59	14.95	1.99
1.5	1.13	3,530	12.97	14.80	1.99
ZnO,2P ₂ O ₅ / water center					
0.00	4.50	2,200	13.50	17.45	2.0
0.25	4.30	2,205	12.83	16.80	2.0
0.50	4.07	2,495	12.30	16.40	2.0
0.75	3.85	2,652	12.14	16.15	2.0
1.00	3.63	2,885	11.83	15.45	2.0
1.25	3.35	3,265	11.72	14.70	2.0
1.50	3.20	3,555	11.97	14.80	2.0

TABLE 47 b

Bonding Agent	Percent anhydrous	Impact Strength inch-pounds	Pyrometric Cone Equivalent
NaAlO_2	2.00	128.3	31.5
$\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2.7\text{SiO}_2$	1.50	98.8	29–30
+ $\text{Na}_2\text{O}, 3.2\text{SiO}_2$	1.13		
$\text{Na}_2\text{O}, 3.2\text{SiO}_2$	1.50	128.3	29
Standard	—	113.7	32–33

The thermal expansion curves were similar for all acceptable binders and were largely determined by the body composition. The standard of comparison was a high grade fired refractory of Missouri fireclay, considered one of the best manufactured in the United States (Fig. 139). They²²¹ have also studied cold setting cements in which they used $\text{Na}_2\text{O}, 2.44 \text{ SiO}_2$ solution (specific gravity 1.56), the solution chiefly used with plastic cements which are to be stored or shipped.



Fig. 139. Both pairs of refractory brick were bonded with the same sodium silicate cement. There was no shrinkage of the fired block on the left compared to the air dried block on the right.

For a composition of 70% pyrophyllite, 10% kyanite, and 20% ball clay the following results were found (Table 48).

TABLE 48

PROPERTIES OF PLASTIC OR COLD SETTING CEMENT (GREAVES-WALKER *et al.*)

$\text{Na}_2\text{O}, 2.44 \text{ SiO}_2$ %	Tensile strength cold set lbs/sq. in.	Drying in cubes %	Fired (Cone 5) (1205° C)			
			Shear lbs/sq. in.	shrinkage	Porosity (apparent)	PCE
5	245	1.2	10	0.9	11.9	26 (1595° C)
10	440	3.6	8	+1.9	21.0	
15	505	1.2	26	0.9	2.6	

The PCE (Pyrometric Cone Equivalent) reached an approximate minimum at 10% sodium silicate and dropped with a straight line relation from the original Cone 32 (1700° C).

The use of dilute liquid phases results in high shrinkage of the finished bond. The overall expansion coefficient may be significantly controlled by choice of the type and amount of aggregates. For instance, cristobalite has a higher coefficient of expansion than does quartz. The effect of shrinkage and expansion may also be controlled to some extent by the thickness of the cement layer. A very thin layer is necessary in laying up refractory bricks.

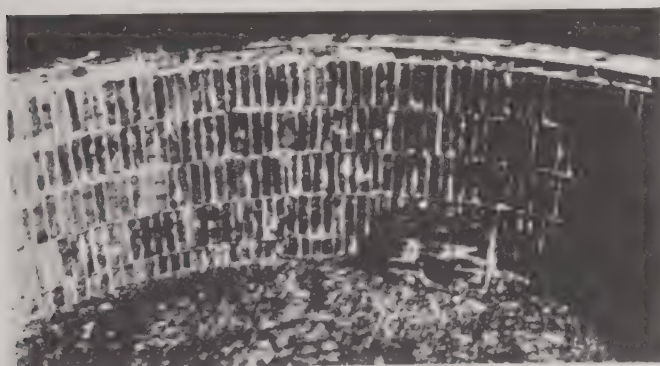
The use of dry powdered silicate in premixed mortars was studied by HEINDL and PENDERGAST²²². They found that a minimum of 7.5% of $\text{Na}_2\text{O}, 2 \text{ SiO}_2$ and 10% $\text{Na}_2\text{O}, 3.2 \text{ SiO}_2$ was required for use with a Pennsylvania fireclay. When mixed for at least fifteen minutes the mortars produced test specimens with a transverse strength of 2500 lbs/sq. inch. The silicates were spray-dried powders containing 17.5% water.

In addition they found that even three months storage in sacks resulted in poor strength related to an increase in CO_2 but after five years in iron drums, the strengths were still at the maximum.

Formulae vary from the soluble silicate solutions alone to mixtures which sometimes appear to be limited by mans' imagination. They are used as refractory cements for laying bricks for boilers, ovens, furnaces, chimneys, and for repairing and protecting stoves, pickling and plating tanks, drains, floors, sewers, etc. For boiler settings the addition of a dilute $\text{Na}_2\text{O}, 3.7 \text{ SiO}_2$ solution is recommended to add some stickiness and prevent the lute of water, fireclay and ground fire brick shrinking away from the bricks. Broken saggers are repaired with 2 parts of $\text{Na}_2\text{O}, 3.22 \text{ SiO}_2$ to 1 part of clay and enough water to give a cream. The bond will set on standing overnight. Ready mixed cements of silicon carbide, fire sand, raw fire clay and powdered hydrated $\text{Na}_2\text{O}, 3.3 \text{ SiO}_2$ are used in large amount for it is usually preferred to purchase materials from manufacturers who have such compounds under continual development.

In the concentrators for sulfuric acid, an acid proof cement for acid

resistant brick is made of fine pure quartz sand and $\text{Na}_2\text{O}, 3.7 \text{ SiO}_2$ in about the proportion of 1 part soluble silicate to 1 part graded quartz. Such construction may require 30 days of air drying for best results. Linings for sulfite digesters used in paper mills, however, take a more alkaline solution. The



Courtesy of Pennsylvania Salt Co.

Fig. 140a. Tank for hot hydrochloric acid lined with brick using acid resistant sodium silicate cement.

$\text{Na}_2\text{O}, 2.4 \text{ SiO}_2$ silicate is added to 1 part of Portland cement and 2 parts of 20 mesh quartz sand. Since the reaction of Portland cement is rapid the mortar is mixed for one brick at a time. Other reactive materials such as metallic sulfides and sulfates may be incorporated. One type with a

controlled reaction time results from forming a gel coating on the reactive particles by pretreatment in sodium silicate. The cement is later prepared by mixing with additional soluble silicate ²²³.

Proprietary mixtures for use in pickling and plating shops which require acid resistance are often mixed on the spot (Fig. 140). One portion may contain a soluble silicate, the other a filler and a substance which will react to cause set independent of evaporation.

In this type, acid resistance and set are obtained rapidly by the use of metallic silicofluoride and fluorides, silicon and its alloys, and similar materials. The cements are so balanced that the products are neutral or acid. It is also important to use a concentrated



Courtesy of Pennsylvania Salt Company

Fig. 140b. Dissolving iron scrap in the finished tank.

silicate solution with a water content found to give the strongest cement ²²⁴⁻²²⁶.

A typical commercial acid-proof silicate cement gaged with liquid $\text{Na}_2\text{O}, 3.2 \text{ SiO}_2$ (38° Bé) will start to set in twenty minutes and reach a final set in about an hour. After a week, the tensile strength will be about 350 lbs/sq. inch, compressive strength 3638 lbs/sq. inch, modulus of elasticity 800,000 lbs. It will adhere to brick, iron or stone with a strength of about 100 lbs/sq. inch which is three or four times the adhesive strength for Portland cement. Shrinkage is less than that of the ordinary slower setting silicate cements. The coefficient of thermal expansion from 25° to 260° C— 12×10^{-6} in./in./°C—approaches that of steel. It loses strength above 400° C and vitrifies at 980° C ²²⁷.

A somewhat preferable formula might use ²²⁸:

93.4 g powdered quartz
4.6 g sodium silicofluoride
2.0 g calcium silicofluoride
30 cc of $\text{Na}_2\text{O}, 2.4 \text{ SiO}_2$ (48° Bé)

The compressive strength is about 7000 lbs/sq. inch.

Another longtime use for silicate cement is in the preparation of abrasive wheels many of which continue to be made by coating each grain with viscous $\text{Na}_2\text{O}, 2\text{SiO}_2$ solution, tamping, air drying and baking at temperatures up

to 300° C. An insoluble bond forms by reaction with clay which is added part by part with the sodium silicate. When silicon carbide grains are used as the abrasive, they react with the silicate binder to form small amounts of hydrogen gas and oxidizing agents are added to such mixtures to take up this gas which would otherwise form bubbles and weaken the bond ²²⁹.

When the melting point of the flux is much exceeded, the charge expands, "bloats", instead of shrinking ²¹⁷.

The preparation of buffing, polishing, and grinding surfaces on fabric discs is accomplished by applying a mixture of abrasive grain in sodium silicate. The usual method has been described by the General Motors Overseas Operations ²³⁰.

A more rapid method, less wasteful of the abrasive grain is to apply the mixture as a spray to the face of the wheel without removal from its place of use ²³¹.

A newer use is the field of binders for welding rod coatings which developed very rapidly prior to the last war. These sheathes prevent atmospheric contamination, control weld composition and cover the joint with slag as insulation. They are complex mixtures and nearly all use either sodium or potassium silicate or both depending on the possibility of contamination of the metal to be welded, tensile strength required, and the need for the smooth arc which is a property of the potassium silicate ^{232, 233}.

Welding rod coatings have been classified by the American Welding Society and the American Society for Testing Materials ²³⁴⁻²³⁵ into series allowing minimum tensile strengths of deposited metal ranging from 45,000 p.s.i. to 100,000 p.s.i. The chemical constitution of the coating is only roughly indicated as "high cellulose potassium" etc.

Table 49 gives compositions meeting the AWS-ASTM series 60 Classifications indicated ²³⁶. The deposited metal has a minimum tensile strength of 62,000 p.s.i.

The patent field is far too extensive to do more than note representatives as an introduction ^{237, 238}.

Gas tight cements for spark plugs have been the subject of much suggestion but at present in the United States the trend is to conductive seals. ²³⁹ The cements require careful handling and carefully sized fillers to obtain the needed density. Water resistance may be increased by treating the exposed surface with an acidic substance. Zinc oxide and calcium carbonate react more slowly.

Other reactive compositions such as magnesium silico-fluoride and sodium silicate with about 90% of ground alumina as filler have been used.

TABLE 49

BASIC COATING COMPOSITION OF THE FUNDAMENTAL ELECTRODES AWS — ASTM
(Allis Chalmers Mfg. Co.)

Coating Material	Electrode Classification					
	E-6010	E-6011	E-6012	E-6013	E-6020	E-6030
Gum and/or resin	3	3	3	3	0	0
Cellulose	1	1	3	2	3	3
Feldspar:						
Al silicates	3	3	2	2	2	2
Clays:						
Al silicates	0	0	3	3	3	3
Talcs:						
Mg silicates	3	3	3	2	4	4
Titanates						
Rutile, TiO_2 , etc.	2	2	1	1	0	0
Fe oxide	0	0	3	0	1	1
CaCO_3	0	3	0	3	3	0
Asbestos	2	2	3	3	4	4
Ferromanganese	2	2	2	2	1	1
K silicates or salt	0	2	0	1	0	0
Na silicates	1	2	2	3	2	2

0 = generally not used

1 = large quantities

2 = medium quantities

3 = small or optional

4 = medium amount or optional

The concentration of the waterglass, presumably Na_2O , 3.2 SiO_2 solution was found to be important. About 30° Bé was satisfactory where high temperature resistance was not required. Where high temperatures were encountered, a solution about 40° Bé was needed ²⁴⁰.

DIETZ prefers to use metal oxides which will form with the soluble silicate self-hardening compositions which will at the same time be infusible at high temperatures and bind the spark plug parts into a unit ²⁴¹.

Numerous combinations of fillers have been used for cements between glass, china or metals. Some such as CaF_2 and CaCO_3 react to form a bond rapidly. Paper soaked in Na_2O , 3.7 SiO_2 may be satisfactory for combining non-porous substances or asbestos may be used particularly where resistance to higher temperatures is desired. Fibers help to avoid shrinkage and maintain the cement in the bond. It should be noted too that coating cellulose fibers with silicate allows their use at higher temperatures as carbonation by oxidation is greatly retarded. They may thus be used up to temperatures at which destructive distillation begins.

There is a myriad of references to the use of sodium silicates in the formation of moldable products. The silicate acts principally as an adhesive

between filler particles. In this group could be listed the whole range of fibrous organic and inorganic materials such as asbestos, sawdust, straw, abrasive grains etc. and many powdered inorganic products²⁴⁷. One large scale use in this group is the briquetting of coal²⁴²⁻²⁴⁴ and soluble silicate also has been used commercially for briquetting iron ore²⁴⁵ and the bath for glass furnaces²⁴⁶. The powdered or fibrous materials are wetted with a dilute silicate usually of highly siliceous ratio since such silicates of soda set more rapidly. The silicate of soda besides providing a positive bond may also control the rate of combustion of the coal briquettes or smelting of the ore briquettes and adds fire resistance to organic fillers.

The reaction of lime with sodium silicate is often brought into play. Brake linings or clutch facings resistant to high temperature are made of wire wound with a fiber having asbestos as its principal constituent²⁴⁸. The fibers are soaked in silicate solution, then in lime or other reactive metal salt solution and then dried at about 100° C to set the compound. Higher temperatures allow variation in the reaction products. Additional binders such as rubber or bitumen may then be added to give resilience²⁴⁹.

Soil stabilization for impermeablizing or strengthening with soluble



Courtesy of Siemens-Bauunion

Fig. 141. The apparatus required for the dual solution system of cementation is shown in this view of a tunnel in preparation for the Berlin sanitation system

silicates or other cement, unlike briquetting, usually depends on some reaction, either with added elements or with the soil to be stabilized. Added elements, acids or salts which will form gelatinous precipitates such as the inorganic acids, NaHCO_3 , Al_2SO_4 , CaCl_2 , are pumped into or mixed with the soil formation following injection of the silicate solution. In some cases the proportions can be regulated so that a single solution containing the reactants can be pumped into the earth formation before gelation occurs. In such a case, the solutions are dilute and the gel-soil structure is weaker than when two more concentrated solutions are used. Where the reaction is with the soil, it may be a result of base exchange with soil clays or other components, or of a reaction such as occurs with loess or dolomite²⁵⁰⁻²⁵². Electrolysis of the formation has also been used to provide reactive ions^{253, 254}. Sand, clay, fissured rock, ash and cinder dumps, diatomite, and masonry are all among the formations which have been treated.

The most widely known uses for the processes are stabilization of soils for building foundations (Fig. 141), sealing water bearing strata in mines, preventing cave-ins from strata of heaving shale or bentonite and consolidating road beds or surfaces²⁵⁵⁻²⁵⁸.

§ 10. DENTAL CEMENTS

For the care and filling of teeth of civilized man, tons of specialized cements are made annually in the United States alone. These cements are not as familiar to the industrial chemist for whom other compositions are better adapted but it is estimated that they are used in 50% of all dental restorations. A dental cement must resist solution by the oral fluids, must have a coefficient of thermal expansion comparable to that of the natural tooth, must have a low heat conductivity, must have a surface similar to that of normal dentine and must be capable of easy molding during placement but set very rapidly once it is in position. These requirements have been most satisfactorily met by "silicate" cements in the form of a ground-up frit of complex composition. It is important to remember that so-called dental "silicate" cements are not simple sodium silicates but rather the powders are finely ground vitrified complexes containing silica. The set cement is the reaction product of the frit and phosphoric acid. These cement powders are mixed with phosphoric acid just prior to use as a filling. Other cements are also used to a lesser extent. The whole subject is very capably surveyed by SOUDER and PAFFENBARGER¹⁸⁹, and their book is the basis of the following discussion.

One of the advantages of a cement is its property of thermal insulation and cement linings are often used in deep cavities for this purpose. Table 50 shows representative values for materials in common use.

TABLE 50

A COMPARISON OF THE THERMAL CONDUCTIVITY OF WELL-KNOWN MATERIALS

Material	Thermal conductivity milliwatts/cm ² /°C/cm.
gold	2940
platinum	696
stainless steel	145
window glass	10.5
dental cement	4.8
hard rubber	1.6

In general, the cements must depend on mechanical factors to hold their position as they do not appear to adhere to the surfaces. Flat sections of teeth and ivory do not show any bond after cement had been allowed to set for 24 hours immersed in water. Restorations are held by mechanical interlocking of the material with the roughened surfaces, and by the frictional resistance of the sand-like particles in the interface.

The dental cements have been classified as

- (1) zinc oxychloride, zinc oxide-eugenol
- (2) copper phosphate, zinc phosphate
- (3) classes 1 and 2 along with silver, copper or mercury salts
- (4) silicate and zinc phosphate – silicate.

Zinc oxychloride is a saturated solution of zinc chloride made up with zinc oxide and cannot be used in contact with soft tissues. It is therefore limited to cavity linings and root canal fillings. With Sorel's cement, they are discussed above.

A mixture of zinc oxide and eugenol is used only as a temporary cement and as a pulp-capping material. In one representative mixture the composition of the powder was 99.8% zinc oxide and 0.2% zinc acetate while the liquid was 100% eugenol. $[C_6H_3(C_3H_5)(OCH_3)OH]$. When used in a ratio of powder: liquid of 2.2 this cement had a setting time at 37° C of 5.5. minutes. After 7 days its compressive strength was 2000 lbs/sq. inch and the solubility test showed 0.7% in the first 7 days. It lost 0.1% as dissolved and disintegrated material when held in water for 7 days.

A more complex composition of this group is

Powder: ZnO	70.25 %
hydrogenated rosin	29.40 %
zinc acetate	0.35 %
Liquid: eugenol	85 %
olive oil	15 %

When used with a powder: liquid ratio of 8.5 this cement had a setting time of 9 minutes and a compressive strength of 5500 lbs/sq. inch after 7 days. Its solubility was only 0.02%.

The copper phosphates contain cuprous or cupric oxide and are used chiefly for their antiseptic value as they tend to have a short life.

The zinc phosphates are used for cementing appliances in place and are more widely used.

A mixture of zinc oxide powder and concentrated phosphoric acid reacts rather violently with intense heat when mixed but in dental work the small amounts used are spread on a chilled slab so that the temperature does not rise above that of the mouth tissues.

TABLE 51

TYPICAL COMPOSITIONS OF ZINC PHOSPHATE CEMENTS AND THEIR PROPERTIES
(SOUDER and PAFFENBARGER)

Sample	B	C	E	F	I	K
Powders						
ZnO	99.7	98.0	92.4	90.3	89.5	88.0
MgO			7.5	8.2	9.4	9.4
SiO ₂	0.1		0.1	1.4	0.3	0.8
R ₂ O ₃	0.1		0.06	0.1		
Bi ₂ O ₃						1.8
Liquids						
PO ₄	55.2	64.3	64.6	52.6	57.9	64.0
Al	3.4	2.7	2.7	2.5	2.8	3.2
Zn	3.1		1.6	7.1		
Mg					0.3	
Physical Properties						
Setting time-minutes	6	8	9	7	10	10
Compressive strength at one week (lbs/sq. inch.)	13,500	12,500	12,500	13,500	12,500	13,000
Solubility and disintegration during first 7 days (per cent)	0.10	0.10	0.15	0.10	0.20	0.20

The relation of the properties of the set cement to the amount of gaging liquid is instructive of the care necessary to obtain the optimum results from any cement.

The setting time of these cements increases as the amount of liquid is increased. For instance, for formula C when 0.25 ml of liquid was used with 1 gram of powder the setting time was 7 minutes whereas with 0.5 ml the setting time was 21 minutes and with 1 ml the cement had not set after 120 minutes. Dilution of the liquid phase also tends to decrease the setting time. In formula C again, the setting time was 21 minutes without dilution whereas when the liquid was diluted 10% by volume the setting time was 8 minutes. The ratio of powder to liquid is very important as a determinant of the final compressive strength. For cement F, for instance, when 1 gram of powder was used with 1 ml of liquid the compressive strength was 5500 lbs/sq inch. When the ratio was 1 gram of powder to 0.5 ml. of liquid the compressive strength was 9000 lbs/sq inch. When the ratio of powder to liquid had been increased to 5 : 1 the compressive strength reached an approximate maximum of 16,000 lbs whereas cement I reached a maximum of 19,500 lbs. These may be compared to the strength of human dentine which has a compressive strength of 30,000 lbs/sq inch whereas strong enamel may exceed 100,000 lbs/sq inch. Amalgams are available having crushing strengths of 45,000 lbs/sq inch. The compressive strength of the zinc phosphate continues to increase with time. Formula F had a compressive strength of 4,000 lbs/sq inch in one hour, 13,000 lbs in one day, 16,000 after 1 week and 17,500 lbs after a month. The compressive strength when stored in distilled water was 9,000 lbs/sq inch after 24 hours and 11,500 lbs after 6 months. At that age after storage in liquid petrolatum its strength was 13,000 lbs/sq. inch. In general there is little difference between storage in distilled water and in oil.

The zinc phosphate cements form a crystalline material when setting whereas the "silicate" cements appear to form primarily colloidal materials of gelatinous nature. While the "silicate" cements are the most widely used they are also considered to be the least permanent of the so-called permanent materials and their primary use is for fillings.

In Table 52 mixtures F and L of silicate-zinc phosphates are included. These latter tend to be even more brittle than the other dental cements and their specific use is as a translucent cementing material.

In general, it may be said of the silicate cements that they are more brittle and about $\frac{2}{3}$ as strong as the zinc phosphate-silicate cements. Their average strength is about 24,000 lbs/sq inch. Most silicate cements appear to reach their maximum strength in about a week when stored in distilled water.

TABLE 52

THE COMPOSITION OF SOME "SILICATE" AND SILICATE-ZINC PHOSPHATE CEMENTS
AND THEIR PROPERTIES (SOUDER AND PAFFENBERGER)

	A	D	F	J	L
Powder					
SiO ₂	47.2	39.9	14.6	39.7	36.5
Al ₂ O ₃	33.1	27.7	15.6	35.8	26.3
CaO	10.4				
Ca		5.9	3.2	3.2	5.9
F		15.4	5.9	11.0	12.0
Na ₂ O	8.7				
Na		6.6	2.9	6.5	4.6
P ₂ O ₅		4.0	2.1	3.9	3.2
loss on ignition %	0.7 (900° C)	0.8 (100° C)	0.1 (120° C)	0.0 (110° C)	6.9 (900° C)
Liquid analyses					
PO ₄ %	60.1	47.4	55.7	48.6	48.1
Al %	1.9	2.3	2.4		1.9
Zn %	7.7	5.6	3.1	8.9	4.4
Mg %			0.7		
Ratio of liquid to powder to produce standard consistency	0.26	0.27	0.26		
setting time at mouth temperature (minutes)	4.0	6.0	4.0		
compressive strength at one week (lb/in ²).	21,350	21,700	28,950		
solubility and disinte- gration during first 7 days (%) *	1.6	1.4	0.8		

They attain somewhat higher strength when stored in saliva and oil. For instance, formula A had a strength of 19,500 lbs/sq inch after 1 week in distilled water and 25,000 lbs in 6 months. Stored in saliva the strength after 6 months was 26,000 lbs while in oil the strength was 30,000 lbs/sq inch.

The ratio of liquid to powder is important as in most cements. At a 0.25 ratio, one cement set in three minutes at 37° C. In one week the compressive strength was 23,000 lbs/sq inch whereas at 0.33 ratio, the setting time was seven minutes and the strength was 19,000 lbs/sq inch.

Shrinkage in 24 hours was 16.5 microns/cm in the first case and 35 in the second. Total solubility in 5 weeks was 2.2% for the first and 3.3 for the second.

Solubility is a very important characteristic of silicate cements since their

* The disintegration during the fifth week was about 10% of the first.

average life expectancy today has been said to be 4½ years. However, “It is not impossible to place silicate fillings which will last 10, 20 or more years.” The solubility loss is greatest in the first week but slowly continues. For instance, in one test a cement lost 3.0% in one week in distilled water at 37° C, whereas in the 4 succeeding weeks it lost on an average of 0.4% each week. As noted above, distilled water is much more corrosive than saliva.

Silicate cements tend to be on the alkaline edge of neutral, about pH 7.5. The pH of course changes with time since phosphoric acid is added to the original frit. Most cements approach neutrality about the end of 24 hours. For instance, the record of one cement showed a pH of 3.5 at 15 minutes, 4.4 at one hour and 5.3 at 6 hours and 5.5 at 24 hours, where the distilled water used as the solvent had a pH of 5.6 to 6.0.

TABLE 53

PROPERTIES OF “SILICATE” CEMENTS COMPARED TO ENAMEL AND DENTINE
(SOUDER AND PAFFENBARGER)

	Index of Refraction	Opacity %	Knoop Hardness kg/mm²
Enamel	1.60	39	267
Dentine	1.56	70	55
Silicate cement (set)	1.45–1.48	25–57	54
Zinc Phosphate cement	—	100	36

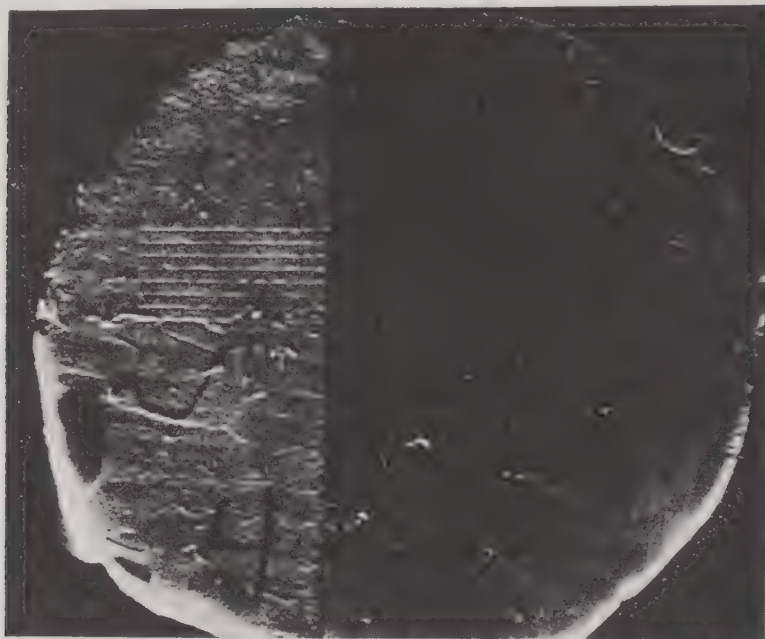
TABLE 54

COEFFICIENT OF EXPANSION (20–50° C) OF DENTAL MATERIALS
(SOUDER AND PAFFENBARGER)

tooth—root	8.3 × 10 ⁻⁶
tooth—across crown	11.4
tooth—root and crown	7.8
silicate cement	7.6
rubber	56.0
porcelain cement	4.1
methyl methacrylate	81.0
platinum	9.0
zinc	29.2
copper	16.8
amalgam (minimum)	22.1
gold	14.4

The net dimensional change of a silicate cement is composed of small internal volume shrinkage in those parts protected from moisture and an expansion in those parts reached by the moisture. Where moisture is

admitted too rapidly over-expansion may result in a soft or spongy layer (Fig. 142).



Courtesy of National Bureau of Standards

Fig. 142. The lighter less translucent half of this disk of "silicate" dental cement was immersed in water two minutes before the time of setting while the darker half was immersed four minutes after the time of setting. As the parallel scratches show, the latter was scarcely affected by soaking seven days while the lighter side was soft and spongy.

§ 11. CONCLUSION

As is the case with many industrial products, there is an extensive literature on sodium silicates which is not readily available to the non-specialist or novice. Much is widely scattered and appears aside from the topic suggested by the main heading. In this chapter we have tried to bring together the information available on the properties of inorganic adhesives and cements and to indicate the location of more specific information on a wide variety of uses. However, space has permitted only a limited bibliography. The manufacturers of industrial chemicals are usually provided with sources of precise information and are glad to answer inquiries.

It would be unfair to conclude this chapter without acknowledging our debt to many members of the Philadelphia Quartz Company who, over the years, have worked in this field and gathered, studied and judged the published literature.

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CHAPTER 7

RUBBERY ADHESIVES

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§ 1. INTRODUCTORY

The tacky nature of a film, prepared from a raw rubber solution, makes the use of rubber as an adhesive obvious and the earliest patents in this field were granted more than a century ago¹. Rubber combines ease of flow (*i.e.* a low yield point) with a high degree of flexibility, but lacks strength, shear and heat resistance. These properties are improved by vulcanization. The development of adhesive solutions based on rubber runs therefore parallel with the continuously changing technique of vulcanization. Many processes in the leather, textile and paper industries, originally carried out with rubber solutions, are now performed with latex, the use of which opens up new fields for rubber as a binder for inorganic fillers and cements. Here again vulcanization is frequently an essential part of the process. Along with these two liquid states of rubber the dry, solid polymer can be transformed into adhesive tape by milling and calender frictioning a thin layer of rubber upon textile or other carrier sheets.

The most important use of rubbery adhesives is, however, their application in the bonding of rubber to metals and to textiles. The sudden change in mechanical properties from an elastomer to a metal has led to a variety of bonding methods, all of which have individual merits. This problem of bonding rubber to metals has recently become further complicated by the appearance of whole families of "elastomers" and plastics on the market, which are all mechanically related to rubber, but have a different chemical structure. A similar extension of possible combinations has resulted from the introduction of rayon and full synthetic fibres into the automotive and textile industries.

In view of the great variety of adhesives and auxiliary compounds discussed in this Chapter, it may be well first to describe briefly those structural relationships which are essential to an understanding of adhesive properties.

§ 2. CORRELATIONS BETWEEN STRUCTURE AND PROPERTIES OF RUBBER ADHESIVES

(a) *Flexibility of Raw Polymers*²

An adhesive film joining a rubber to a rigid material can have the mechanical properties of either component or, preferably, intermediate properties. In laminating flexible materials, such as paper, leather or textiles, the adhesive film must be flexible as well. It has been found in recent years that the limiting temperature at which a polymer breaks on rapid deformation is a characteristic constant depending essentially on the properties of the molecular units. Rubbery adhesives can be divided roughly into two classes, according to the value of their "brittle point" temperature. Those with a low brittle point (Table 55) are flexible, but usually have little tensile strength and shear strength in the unextended state, while the second group (Table 56) consists of plastics with a high yield point which are rigid at 20° C.

It is clear from Table 55 that the brittle point of all elastomers is well below 0° C. The lowest value for polybutadiene is gradually raised by the introduction of voluminous (CH_3) or polar (Cl) substituents, copolymers with bulky (C_6H_5) or polar (CN) groups producing the same effect. Two plastics are included in this series: polyethene and gutta-percha. They are crystalline up to about 60% and therefore possess a high yield point but share the flexible chain with the rubbers.

Polar groups, present in many vinyl polymers as well as in chlorinated rubber, raise the brittle point. Cyclization of the rubber chain leads to a loss of molecular mobility and therefore also to a higher brittle point, which may be raised to more than 100° C above that of rubber, depending on the degree of cyclization. A large crystalline fraction determines the film-forming properties of rubber hydrochloride. The rigidity of these adhesive films is reduced by small quantities of plasticizers or solvents, or by the admixture of other polymers. As traces of solvent are retained with obstinacy by the film and since these adhesives are applied as cements, it is likely that they contain sufficient solvent acting as a plasticizer to make them flexible at moderate temperatures. These adhesives are closely related to the synthetic thermoplastics discussed in the foregoing Chapter.

Whereas the mechanical properties of the adhesive film are readily understood, we have only a rough picture of the relation between structure and tack. Polyethene lacks all adhesive power, whereas gutta-percha is, like natural rubber, an excellent adhesive. It is probable that the small quantities

TABLE 56

BRITTLENESS OF RUBBERDERIVATIVES AND RELATED PLASTICS

Name	Structural units	Crystallinity	Brittle point °C
Cyclized rubber	$ \begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2- \\ \\ \text{C} \end{array} $	Amorphous	+60 — +100
Polystyrene	$ \begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}- \\ \quad \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array} $	Amorphous	+80
Rubber hydrochloride	$ \begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}_2- \\ \\ \text{Cl} \end{array} $	± 60% at 20° C	+90
Chlorinated rubber	$ \begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}-\text{CH}-\text{CH}- \\ \quad \quad \quad \\ \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array} $ <p>schematic</p> <p>+ partly cyclized rubber groups</p>	Amorphous	+60 — +80
Polyvinylchloride	$ \begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}- \\ \quad \quad \\ \text{Cl} \quad \quad \text{Cl} \end{array} $	Amorphous	+80

of oxygen, which are always present in olefinic polymers as $-OH$ or $-CO$ groups, contribute to their tackiness. GRS, however, which is also olefinic and contains some oxygen, has no adhesive power at all and polyethene contains similar quantities of oxygen, which obviously lack all efficiency. Some unknown property, perhaps differences in the ease of flow of thin polymer films, must be decisive for the adhesive properties of a raw polymer.

(b) *Vulcanization and Ebonite Formation*³

Cross-linking of an elastomer leads to a reduction of the plastic flow, increases the rate of elastic recovery and the modulus. Although many cross-linking agents exist, the only one used in industrial practice is sulphur. Sulphur groups in the rubber unfortunately induce oxidation and are therefore kept at a minimum in a modern rubber vulcanizate. For the purpose of this Chapter it suffices to state that curing formulas for natural rubber, GRS and the nitrile rubbers are very similar, while Neoprene cross-links on heating even in the absence of sulphur. There are three components essential to a rubber mix, *viz.*, 1–3% sulphur, 0.5–2% of an organic accelerator and zinc soaps formed from zinc oxide and fatty acids, which are partly present as a natural impurity and are added as non-volatile fatty acids, stearic acid being the most widely used. Accelerators are compounds capable of activating the sulphur (probably by the intermediate formation of loose complex compounds) to such a degree that rapid reaction with olefines can occur between 20° and 150° C. Certain sulphur-containing accelerators (Thiuram) are capable of vulcanizing rubber even in the absence of free sulphur. The vulcanizing temperature depends on the type of accelerator used. Table 57 gives the principal properties of the accelerators mentioned in this Chapter.

Sulphur chloride produces cross-linking in rubber cements at 20° C

TABLE 57
NAME, COMPOSITION AND ACTIVITY OF ACCELERATORS

Trade Name	Chemical composition	Vulc. time at 142° C, minutes	Application characteristics
D.P.G.	Diphenylguanidine	45	Cheap
Captax	Mercaptobenzothiazole	20	Normal
Altax	Benzothiazyl disulphide	20	Slightly delayed action
Santocure	Captax – amine complex	20	Delayed action
T.M.T., Tuads	Tetramethylthiuram disulphide	5	Ultra accelerator
Methyl zimate	zinc dimethyl dithiocarbamate	3	Activator for Captax-Altax
Butyl zimate	zinc dibutyl dithiocarbamate	2	Ultra accelerator for latex

within a few minutes and is still used in the curing of articles having a thickness of less than 0.5 mm. It is, however, difficult to avoid bad aging of these vulcanizates and the lachrymatory properties of the vulcanizing agent are a drawback to its technical application.

Fillers can be added as cheap diluents. Most fillers increase the modulus of the vulcanizate more or less, the carbon blacks being outstanding in this respect. It should be borne in mind that this reinforcing effect of active fillers is a function of temperature and is less pronounced at 70–100°C.

Rubber heated with 12–20 parts of sulphur yields a leathery product with a strong tendency to oxidize. It is a useful adhesive interply in structures which are not in contact with air. The reaction product of rubber with 30–40 parts of sulphur is black "hard rubber" or ebonite. Diffusion of oxygen through the rigid polymer is slow and, as there are only a few double bonds left, this derivative has excellent resistance to oxidation.

The fact that the function of sulphur in low concentrations is essentially that of a cross-linking agent, has frequently led to the misconception that hard rubber owes its mechanical properties to a large number of cross-links. The correct interpretation of all observed facts produces a quite different picture, *viz.*, the structure of ebonite is closely related to that of cyclized rubber; see Table 56. Ebonite swells strongly in chloroform and similar solvents. Taking the high cohesive energy density into account, the degree of cross-linking should not differ much from that of a soft rubber vulcanizate. A high impact strength (average 40 kg/cm², maximum 100 kg/cm²) supports these contentions. The hardness of ebonite is due to the same cause as that responsible for the hardness of cyclorubber, namely the rigid ring structure. The presence of polar sulphur groups enhances this effect. Hard rubber begins to soften above 60° C, which again is in agreement with the assumed formula of a sulphurized cyclorubber. These thermoplastic properties limit the use of this versatile adhesive.

(c) *Isocyanates* ⁴

This important new class of rubber adhesives has been discovered recently by the chemists of I.G. in Germany. Isocyanates are prepared by the interaction of an organic base and phosgene. The isocyanate group R—N=C=O is extremely reactive with compounds containing active hydrogen. With water, for instance, the reaction product is a substituted urea:

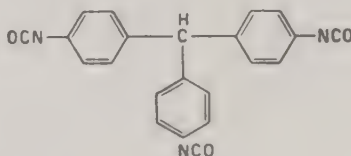


This reaction can be used to build up long chain compounds and in the course of such research it has been incidentally discovered that the isocyanate

group has excellent bonding properties. The compounds used at present are tri- or bifunctional monomers, which may be polymerized slightly on application, but are actually cross-linking agents, giving three or two dimensional structures respectively. The technical trend at present aims at "delayed action" or "masked" isocyanates, which would be easier to handle in the presence of moisture and at elevated temperatures.

Isocyanates mentioned in this Chapter are:

- (1) The original German Desmodur R, a crystalline material, soluble in methylene chloride,



- (2) The aliphatic H.D.I. is a free-flowing toxic liquid,



- (3) An (aromatic?) product from I.C.I. of undisclosed composition, Vulcabond TX, is a crystalline body soluble in aromatic and chlorinated solvents,



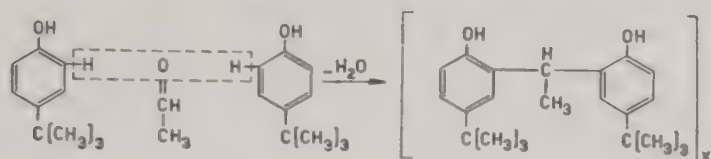
(d). *Tackifiers and resins*

In rubber technology two types of adhesive bonds are essential. One, a strong permanent bond, is produced by one of the compounds discussed in group a-c; the other type of bonding described by the term tackiness will be considered now. Tackiness implies the rapid formation of an adhesive bond, the strength of which may be either equal or much inferior to that of a permanent bond. In building laminated structures like tyres or belting, a temporary bond, sufficient to hold the plies together until they are vulcanized, will often be all that is needed, the main requirement being that adhesion between the surfaces shall take effect immediately under only slight external pressure.

Natural rubber has tack for many surfaces but sometimes tackifiers like resin, coumarone resins or asphalt are added. The common feature of these agents seems to be a molecular weight between 200-1500, a rigid structure like that of cyclo-rubber and the presence of at least some polar or hydrogen bonding groups. The lack of tackiness in GRS and Buna S cannot be compensated for by these auxiliary ingredients, but a new group of resins

has been discovered by REPPE and his colleagues and further developed in the United States ⁵.

It was stated originally that "Koresin" is the condensation product of tert. butylphenol and acetylene. The reaction becomes more obvious by writing the hydrate of acetylene, *i.e.* acetaldehyde thus:



Only the resins prepared in acid solutions develop the typical tackifier properties. Those from alkaline solutions are chemically similar, but infra-red analysis shows that hydroxylic end-groups, which are essential for the formation of adhesive bonds, are probably lacking. The molecular weight of the resin is another critical property. Furthermore, it seems to be easier to substitute acetaldehyde by crotonaldehyde or formaldehyde (Arofene 775) than to change the phenolic constituent. Koresin, however, seems to represent the optimum balance of properties with GRS.

The following hypothesis may be helpful towards explaining the valuable properties of Koresin. Many phenolic resins are good adhesives. To combine them with GRS they must be able to form a mechanical mixture with the rubber and must form a film of some rigidity. Brittleness of the resin films is overcome by the elastic backbone formed by the rubber. Mixing of rubber and resin depends on the molecular weight of the resin, the rate and degree of hardening, *i.e.* the previous history of the resin, while the brittleness of the resin film depends also on the flexibility of the elementary units of the resin. These factors must be balanced against the hydrogen bonding or polar groups, which provide adhesive properties.

Koresin was worked out chiefly to solve the specific problem of building tyres from GRS. Elastomer resin combinations seem to gain prominence in a much more general way. Nitrile rubbers combined with phenolic resins are excellent bonding agents. This bonding power is less sensitive to the composition of the resin, but the nature of the bond is closely related to that of Koresin.

§ 3. MEASURING THE STRENGTH OF A RUBBER ADHESIVE BOND ^{6a}

The value of a rubber mix under many service conditions can be fairly accurately predicted on the basis of mechanical tests, although the mecha-

nical and aging properties of a technical rubber vulcanizate may be 20–30% lower than those inferred from the laboratory test mix. The most important factor is the poorer dispersion of compounding ingredients when mixing takes place in a factory. By contrast, the testing of a rubber adhesive bond gives only a rough picture of its properties. This is due to the fact that bonding in a laboratory can be done more accurately than in a factory, that the adhesive bond is less homogeneous than a piece of rubber and finally that a static test gives no information as to dynamic fatigue of a joint. Even adhesion test pieces prepared with the utmost care in a laboratory may give totally unexpected rejects and factory-produced adhesion shows this defect in a much larger percentage.

Conventional tests exist for classifying the viscosity, stability, cold brittleness and drying time of an adhesive cement. The resistance of the joint to corrosive chemical reagents, artificial and natural light and heat can also be determined by standard exposure tests. Bond strength can be determined by one of the following three types of static methods, which are modified sometimes for special purposes.

(a) *Measuring the Absolute Value of Bond Strength by the Pull Test*^{6b}

This method is an adaptation of the classical tensile strength test to rubber. It is used mainly for testing the adhesion of rubber to metals, but has recently been modified for the study of fibre-to-rubber bonding.

Adhesion of rubber to metals can be produced by one of the four different groups of adhesives discussed in § 5. For testing, a cylinder of rubber is vulcanized in a mould between two metal parts according to the specification given in Figure 143. The specimen is properly centred in a conventional tensile strength testing machine, with a capacity of 10000 lb. The total pull at rupture is recorded and expressed in lb/sq.inch or kg/cm² of the adhesive surface. There should be at least two vulcanizations of three test pieces each. The deviation from average for six samples is liable to be very large⁷, and is still larger in factory experience; it may be considered to be of the order of 30%.

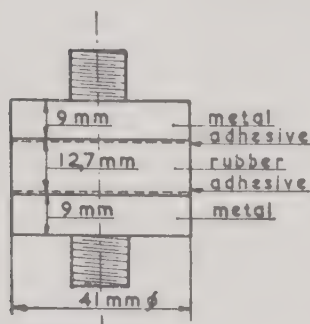


Fig. 143. Dimensions of a metal-rubber test piece used in the evaluation of adhesive bond strength in a pull test.

A test in which a standard piece of wire is vulcanized with a rubber sample and pulled out under standard conditions may be useful for special purpose testing. Pull tests designed to measure the adhesion of rubber to cord are based on a

similar principle. In the "H" test a single cord is pulled out of a block of rubber and the shear stress measured. Its reproducibility is low, but the test is useful for plant control of dipped tyre cord ⁸.

The absolute value of the adhesive bond at room temperature is highest for ebonite and may reach 100–150 kg/cm². The strength of rubber to metal bonds is usually between 40–80 kg/cm² and 20 kg/cm² is considered a permissible lower limit.

From Table 24, p. 244, we learn that plastics adhere to metals with a strength similar to that of ebonite ⁵ (100–250 kg/cm²), while raw Neoprene and rubber give a bond comparable to that of the weaker adhesives (12–30 kg/cm²). The tensile strength at break of a high-grade natural rubber is 10 to 40 times higher (2500–4000 kg/cm² relative to the actual cross section). Two causes for this difference may be mentioned. In the first place, the high tensile strength of rubber is that of a thin standard test piece, whereas a specimen cut out of a thick piece of rubber gives much lower values. In the second place, unfavourable strains are produced on the edges of the rubber-metal bond due to the enormous difference in modulus between the two materials. A highly loaded rubber with a correspondingly higher modulus therefore produces about 50–100% higher values in the test for the same adhesion bond. This is illustrated by Fig. 144 based on experiments

with chlorinated rubber. A pure gum vulcanizate separates under a pull force of 20 kg/cm², for a rubber reinforced with 44 parts of carbon black 70 kg/cm² is necessary, but on further addition of filler the strength of the bond is reduced, probably because the interface is now starved of the hydrocarbon component.

Some information on the cause of bond failure can be gained from a

study of the fracture, which can be located either in the rubber or at the ply. When high-grade rubber compounds are used, failure occurs at the

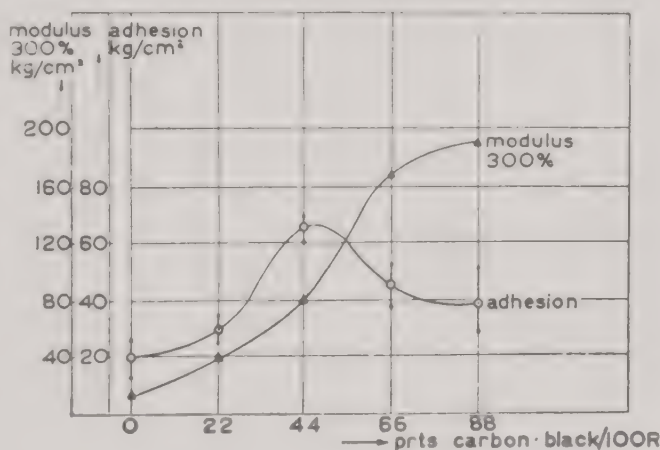


Fig. 144. Influence of carbon black concentration and modulus on strength of adhesive bond. Pull test, mean value of 6 test pieces. Typly Q (chlorinated rubber adhesive), thickness of layer about 10 microns, natural rubber to steel.

rubber-metal interface and not in the rubber. With ebonite interplies, the ebonite separates from the metal; when cyclorubber is used, failure occurs in the adhesive, while chlorinated rubber mostly sticks well to the metal and failure occurs here essentially between the rubber and the adhesive. In brass-plated joints the rubber is, of course, separated from the brass.

(b) *Relative Values obtained from the Friction and the Shear Test*

The stripping of a sheet of rubber or rubberized canvas cemented to a metal surface (see Fig. 145), gives, in principle, the same result as the pull test⁹. Reproducibility, however, is much better. This is due to the fact that failure of the bond at one point does not affect the bonding of the residual sheet. One can see this effect from a diagram (Fig. 146), in which the actual stripping forces in kg per inch width of the test piece have been registered. It is seen that the variation in tensile strength is considerable, but an average value can be interpolated from the graph. Two precautions are necessary: soft pure gum mixes have to be vulcanized with a strip of canvas and friction between rubber to rubber at point B in Fig. 145 has to be reduced by wetting with glycerine. Results are then reproducible to within 10%.

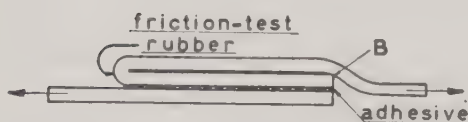


Fig. 145. Friction test, for significance of lubrication at point B, see text.

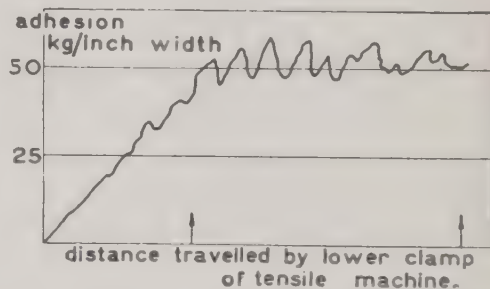


Fig. 146. Friction test, example of registration on a Schopper Dynamometer, Rubber-carbon black mix to metal. Value derived from graphic integration between arrows.

In testing rubber-canvas adhesion, a strip of woven fabric is peeled away from a rubber-fabric sandwich. Although the forces expressed per unit width are not well defined, this accurate method is widely used, because the coefficient of variation for the "H" test mentioned above is at least six times greater. The rate of peeling impresses itself strongly on the measured adhesive strength and must therefore be accurately given. Specified peel tests are used for testing rubber-coated fabrics, friction tape and rubber hose.

The shear test is a suitable method for measuring a great variety of materials (see Chapter 9). Although absolute values, similar to those obtained by the pull test, are measured, their value depends somewhat more on experimental conditions. A special method, which is essentially a shear test, consists in bonding two concentric metal rings by a layer of vulcanized rubber.

(c) *Dynamic Fatigue*

A number of machines for testing the dynamic fatigue of rubber, rubber to metal bonds, fabrics or even whole tyres have been constructed¹⁰. The principle underlying the design is that a rubber can be given an initial stress and then undergoes a periodic deformation, which can be either a compression or an extension. The essential point is not only the sudden change in load or extension (compression), but the evolution of internal heat, which is due to the hysteresis shown by all loaded elastomers on plastic-elastic deformation. Moreover, failure of the adhesive bond due to dynamic fatigue may be caused by differences in the modulus of elasticity for the two construction materials. It will be shown in the section of rubber-to-fibre bonding that such dynamic fatigue tests give more than 10 times greater differences between two similar bonds than those revealed by the static tests. The evaluation of adhesive rubber bonding in vibrating constructions will therefore remain partly a matter of trial and error until dynamic testing can be standardized and placed on a sound physical basis.

§ 4. FLUID ADHESIVES

(a) *General Remarks*¹¹⁻¹⁶

An elastomer can be used either in an organic solution (cement) or as an aqueous suspension (latex); both types of adhesive are applied in an uncured as well as in a vulcanizable form. The bulk of all rubbery adhesives belongs to one of these four types of liquids made up from natural rubber. Recently Neoprene, GRS, and nitrile rubbers in combination with other polymers have been added to the list of basic materials for adhesives (*cf.* list of patents at the end of this Chapter).

At a rough estimate, probably about 5% of the world's rubber consumption is used in adhesives. This would be about 50,000 tons annually of dry rubber and about 2000 tons of latex. More than half of these quantities is applied in tyre production. An accurate estimate is not possible, as adhesives are mostly prepared in rubber factories for consumption on the

spot. The essential difference between latex and solutions is the low viscosity of the former. Latex with 40% rubber is about 100 times less viscous than a 10% rubber solution in benzene. Both viscosities can be measured by a penetration method or with a Höppler viscometer.

Latex-based adhesives are used to join leather to leather, crepe rubber soles to leather, felt to leather, rubber to fibres, paper to paper, and as binders for inorganic fillers. Latex processing is very simple. The basic material can be purchased ready for use, stored (above 0° C) for an unlimited period, the concentration can be adjusted from 60% downward by dilution with water and its application involves neither fire risk nor health hazards. Latex adhesives are therefore rapidly taking the place of rubber solutions wherever possible. The 20–30% higher price of rubber in the form of latex is offset many times over by these advantages. Limitations are imposed by a number of apparently minor factors. Latex must be handled free from dust and talc, processing should therefore be separated from other sections of the rubber factory. Shipments of different lots are not identical in colloidal properties, *e.g.*, rate of coagulation. The small consumer therefore encounters difficulties in standardizing processing, but with large-scale use, homogenizing by storing in bulk becomes possible.

Vulcanizing latex is used in tyre production, in making canvas for V-belts and in combination with paper, *e.g.*, cardboard, where a yellow colour on aging is not objectionable. Unfortunately, vulcanization of latex is still an obscure art, which upsets many of the attractive factors just mentioned. Two suspensions, the latex and the vulcanizing ingredients, have to be mixed under accurately standardized conditions, stability of the latex mixture as well as the rate of vulcanization being very sensitive to small changes in the formula.

Raw rubber solutions compete at present in the footwear industry with nitro-cellulose lacquers and vinyl polymers as adhesives for the production of a temporary bond. A fast-drying binder with a low-boiling solvent is frequently desirable. Non-inflammable solvents, such as trichloro ethylene, are expensive and highly toxic and therefore objectionable in mass production processes. Concentrated (20%) rubber solutions are difficult to handle and their preparation involves heavy milling, leading to a degraded rubber with inferior film-forming properties. On storage the viscosity of such solutions tends either to decrease or the polymer may settle out as a gel, both types of aging being caused by oxidative reactions. Raw rubber solutions are used for joining rubber to rubber (if thermoplasticity of the joint is not objectionable), rubber to leather and for cementing rubber and linoleum flooring to the ground. Modern shoe repairers execute work on footwear

with the aid of rubberized adhesives where riveting or machine sewing would be very difficult or in some instances quite impossible.

Vulcanizing solutions are definitely easier to handle than the corresponding latex systems and are widely used in rubberizing textiles, in manufacturing hoses and in the rubber industry in general. The frictioning of dry rubber on a textile base is a competitive method in the production of adhesive tape (see § 6).

Latex can be applied by brushing on small areas or by spraying large, rough surfaces. Only brushing or picking up from dipping rollers can be used for the application of solutions. A smooth clean surface is in any case very essential. Cleansing with a solvent or mechanically with abrasive paper, with brush, sand or shot blasting are the conventional techniques employed.

It is very important that adhesives should be used correctly. The application of an adhesive in solution to two surfaces which do not allow the solvent to escape, leads to low adhesion figures unless the film is dry. In cases where creep of the adhesive is objectionable, a thin film should be used.

Simple polarity considerations are a sufficient guide in the choice of an "oil-resistant" joint between a polar and a less polar polymer. Sometimes only a weak temporary bond, such as is produced by raw rubber, is required. In shoemaking operations it must be possible to unstick a faulty bond. In tyre production, on the other hand, a firm bond between rubber and fibre is produced by vulcanization. For certain elastomer-fibre combinations cross-linking with the aid of isocyanates becomes preferable. It is obvious that a special rubber adhesive serving all purposes cannot exist, but a combination of two polymers, preferably on a nitrile rubber base, goes a long way towards realizing that desirable end.

(b) *Adhesives based on Latex*

Natural rubber occurs in the form of globules with a diameter of 1–3 μ . They are kept in suspension in the serum by a layer of proteins. Fermentation processes are prevented by the addition of ammonia. The serum and the rubber globules contain natural antioxidants, which retard oxidation, and fatty acids, which influence the rate of vulcanization. Either concentrated latex of about 60% dry rubber content or ordinary 40% latex is available. Latex from the rubber-producing countries is shipped almost without exception in a concentrated form and in the latex-consuming countries the desired concentration is obtained by dilution with water.

Alginates can be added as thickening agents, but cause undesirable creaming on standing and retard the drying of the adhesive layer. A high

viscosity of the adhesive is, however, useful for the covering of rough surfaces. The drying process can also be lengthened by the addition of 10–20 parts of glycerine or starch musilage. These hygroscopic layers are useful in shoemaking. Tackifying agents, which weaken the adhesive strength but increase the stickiness of the layer, can be added in the form of dispersions of resins or oils. Addition of borax-casein sometimes improves the adhesive bond. Another means by which tack can be enhanced is by adding an emulsion of a rubber solvent, *e.g.* toluene, to the latex. The adhesive layer can be stiffened by the addition of bentonite, but this is hardly to be recommended, as it greatly reduces the adhesive power of the latex¹⁷. In some cases, when the thickening effect of the clay is objectionable, mica powder is used instead to impart the necessary stiffness to the adhesive layer.

The already weak adhesion of a rubber film to glass or steel is reduced still further by the addition of caustic soda to the latex, but, curiously enough, a mixture of Revertex (60% latex stabilized with soap) and cement is an excellent adhesive for joining glass to steel. It can be used as a binder for many fillers, such as sand, wood chips, cork granules, ground rubber waste, etc. Such mixtures are applied as flooring and as non-skid surfaces¹⁸. Many attempts have been made to impart more strength to the adhesive layer¹⁹ but coumarone resins, shellac or reclaimed rubber improve the tack rather than the adhesion. The application of phenol-formaldehyde resins formed in ammoniated latex has been reported; it is likely that the resin contributes more to the adhesion process than the rubber. In fact, the combination of resorcinol resins with latex has gained prominence in the treatment of rayon cord, and similar combinations with GRS-latex have been mentioned.

Synthetic latices from butadiene^{20, 21} are among the compositions studied by German authors during the war but were found to be inferior to natural rubber. Casein has to be added in order to obtain at least some adhesion. The tackiness of Neoprene latex (type 571) is also negligible, but a special-purpose product (type 572) has been put on the market.

Vulcanization can be produced in the adsorbed rubber layer by addition of a prepared suspension of the ingredients to the latex. The rate of vulcanization depends essentially on the accelerator, and may vary from minutes to days. Some examples are given in Table 58. Near room temperature only slow-curing mixes are easy to handle, whereas an adsorbed layer can be vulcanized on drying at 100–120° C in minutes. Vulcanization imparts strength to the rubber film, but does not improve the adhesive bond with fibres, leather or metals to any appreciable extent. There is,

however, one notable exception. A cured latex-haemoglobin mixture adheres much better to metals than does an ordinary vulcanized latex film. Oxidation, not vulcanization of the rubber, causes this improvement, as will be discussed in § 5.

TABLE 58
VULCANIZING LATEX MIXTURES
(quantities in parts by weight)

Example 1. A fast curing mix for frictioning laminated canvas in the production of rubber hoses

Rubber (60% latex)	100	<i>Vulcanization time</i> at 110° C about 10 min. 70° C about 4 hours
Zinc oxide	2	
Antioxidant	1	
Sulphur	2	
Butyl zimate	1	

Example 2. A slow curing mix for bonding canvas to rubber in the production of tyres

Rubber (60% latex)	100	<i>Vulcanization time</i> First phase: slow drying to allow condensation and hardening of the PF-resin at about 120° C. Second phase: Vulcanization together with the rubber layer bonded to the canvas about 30 min. at 142° C.
Zinc oxide	5	
Antioxidant	1	
Sulphur	2.75	
Captax	0.8	
Stearic acid	1	
Resorcinol	20	
Formaldehyde	12	
Caustic soda (catalyst)	2	

Emulsions of reclaimed natural rubber are sometimes added to replace about 30% of the latex. This is done for economy and has no technical advantage. GRS and Buna S latices have smaller particles and therefore penetrate better into the fibre. The adhesive film, however, has very little tack. Casein has to be added to produce bonding of practical value. Actually the adhesive consists of a casein film, which has been made pliable by the addition of GRS. Nothing has been published on the value (if any) of Perbunan latex for this purpose. Thioplast-latices, which have been mentioned in literature, are useless in practice. Neoprene latices, improved by the addition of casein, hydrogenated natural resins or aldehyde-amines find a limited application for the bonding of elastomers to metals and glass.

(c) *Adhesives based on Rubber Solutions*

A rubber solution can be prepared from masticated crepe, sheet or reclaimed rubber ²². Lower qualities, such as slab rubber or flat bark rubber, contain

more resinous impurities, which tend to increase the stickiness of the solution but at the same time induce excessive oxidation²³. Milling of the rubber leads also to an oxidative degradation, but is necessary for the production of a concentrated solution²⁴. "Dead milled" rubber on the other hand yields a poor adhesive. Tack and hardness are improved by the addition of coumarone-indene resins, shellac, ester gum or hydrogenated resin, but care must be taken to avoid induced oxidation on storing. A few units per cent. of oxygen may improve the molecular interaction of rubber with polar surfaces, but rubber containing 10–15% of oxygen forms a brittle film. For this reason the addition of rosin, which produces peroxides with air, is undesirable. Economy governs the choice of a solvent²⁵, that commonly used being naphtha, benzene or gasoline. In some countries the use of benzene is prohibited because of its toxic properties. The boiling point of the solvent obviously influences the rate of drying, in addition to which the diffusion of solvent residues through the joint has to be taken into account.

A patch of vulcanized rubber sticks to the surface of, *e.g.*, the inner tube of a bicycle tyre with the aid of a few drops of rubber solution. Traces of solvent serve first as a softener and help to distribute the raw rubber adhesive between all the microscopic irregularities of the two surfaces. Gradually the solvent diffuses through the vulcanized rubber and the adhesive bond between the two surfaces does not gain full strength until considerable time of drying has elapsed. Conditioning of drying, starting with slow drying, is therefore an important factor in the production of permanent adhesive bonds. Similar considerations have to be taken into account in the design of adhesive tapes.

Polar solvents do not dissolve natural rubber, but a small percentage of anhydrous alcohol added to a rubber solution in naphtha lowers its viscosity. The association of rubber molecules dissolved in, *e.g.*, naphtha is partly due to dipole interaction between the small quantities (1–2%) of CO, OH and COOH groups, which are formed in the rubber during mastication. Alcohol solvates these associates and therefore reduces the number of secondary valency contacts between the chains.

The use of vulcanizing solutions introduces a number of unavoidable complications. Two batches have to be stored: (a) the raw rubber solution, (b) the vulcanizing ingredients. After mixing, incipient vulcanization is indicated by gelation and the "activated" mix has therefore to be used within a few days or even some hours. Gelation can be retarded by the addition of nitro-paraffins²⁶ but this poisonous stabiliser will also influence the drying time of the adhesive.

The rate of curing is essentially a function of the type and quantity of accelerators used. At room temperature it should be days, at 120° C, minutes. Table 59 gives some representative examples. Ultra accelerators naturally increase the danger of premature gelation²⁷. Chlorinated solvents produce traces of HCl, which acts as a retarder. This, in turn, can be compensated for by the addition of weak bases or aldehyde amines, which at the same time activate the accelerator.

TABLE 59
VULCANIZING NATURAL RUBBER SOLUTIONS
(quantities in parts by weight).

Example 1. A slow curing solution for frictioning hospital sheeting.

Rubber	100	Solution: 20% in naphtha.
Stearic acid	0.5	Vulcanization in 2 phases.
Antioxidant	1	First phase: gradually rising in hot air
Zinc oxide	5	for 60 min to vulc. temperature.
TiO ₂ (white filler)	40	Second phase: 90 min at 130° C.
Whiting (cheap filler)	25	
MacNamee clay (stiffening filler)	25	
Sulphur	0.75	
Captax (accelerator)	1	
Methyl zimate (booster)	0.25	
Telloy (tellurium)	0.5	

Example 2. A slow solution for building up rubber canvas (except for tyres).

Rubber	100	Solution: 10—15% in naphtha.
Pine oil	1	Vulcanization: under pressure or wrapped
Stearic acid	1	in cotton, 15 min at 142° C.
Antioxidant	2	
Zinc oxide	5	
Sulphur	2.5	
Altax (accelerator)	0.5	
Methyl zimate (booster)	0.1	

Example 3. Fast vulcanizing solution for curing at 20° C.

Prepare separate solutions A and B.**

Solution 10—15% in naphtha	A	B	Pot life of activated mixtures A + B
Rubber	100	100	about 4 days at 20° C.
Zinc oxide	5	5	Vulcanization time: 6 days at 20° C.
Zinc stearate	1	1	
Antioxidant	1	1	
Butyl zimate (ultra accelerator)	2	—	
Butyl aldehyde aniline (accel.)	2	—	
Inactive carbon black *	2	—	
Sulphur	—	4	

* Carbon black is added as colouring matter to control homogeneity of mixture A + B.

** Alternative method: spread mixture except ultra-accelerator, add a lower concentration of the latter after drying of the first layer.

The viscosity of the cement can be increased by reinforcing fillers, such as carbon black or clay. Any addition of coarse particles, however, will tend to endanger the smoothness of the adhesive film. Blooming of sulphur, anti-oxidant or poor dispersion of the ingredients are similar sources of trouble.

It has already been mentioned in § 2 that GRS lacks all tack. The addition of 10–15 parts (relative to the rubber) of Koresin to a solution of GRS remedies this shortcoming, wherever GRS is preferred above natural rubber for economic or political reasons. Patents claim the application of other hardening resins, related chemically to Koresin, in combination with GRS. Mixtures of GRS and natural rubber have been proposed for vulcanizing solutions; their technical value, however, is obscure. The natural rubber component vulcanizes more quickly and the GRS-fraction has therefore only the function of an expensive plasticizer. Sodium polymerized polybutadiene (Buna 85) has more tack, but the film lacks the strength necessary for most purposes.

Cements based on Neoprene-type rubbers^{28–30} are preferable to natural rubber solutions in a number of special applications. The bonding of polar rubbers or plastics, the production of an oil- or grease-resistant bond for attaching tank lining or chemical-resistant adhesive bonds, can all be produced with advantage from a Neoprene solution. The much higher price of Neoprene compared with natural rubber on a volume basis militates against the use of the former as a “general purpose” adhesive.

The “oil resistance” of Neoprene must not be overrated. The term refers only to paraffinic solvents, for aromatic liquids swell a Neoprene film in a marked degree. Neoprene is less susceptible to oxidative degradation than natural rubber. This property is useful in rubberized fabrics but is of little account in joints which are not exposed to air and light. The presence of polar groups impairs the electrical properties of the film, but aids the penetration of the solution through porous surfaces.

Concentrated solutions of Neoprene are more susceptible to gelation than those made from natural rubber. Storage times range between some weeks and 5 months, depending on the type of Neoprene used. The viscosity can be controlled by milling similar to the mastication of natural rubber, although breaking down on the mill has much less effect on the properties of the adhesive film with Neoprene than with natural rubber. Aging of the film leads to cross-linking, *i.e.* auto-vulcanization, and makes the originally uncured film superior to the uncured natural rubber film. For this reason the application of vulcanizing solutions is of less importance. Moreover curing occurs in the absence of sulphur on addition of magnesia, zinc oxide or special curing agents; see Table 60.

TABLE 60
VULCANIZING SOLUTIONS OF NEOPRENE
(quantities in parts by weight)

Example 1. Slow curing cement

Neoprene type S.C.	100	Dissolve 25 parts in 75 parts benzene. Vulcanization: 30 min at 140° C.
Extra light calcinated magnesia	4	
Zinc oxide	5	
Semi-reinforcing carbon black	30	
Neozone A (special antioxidant)	2	
Stearic acid	0.5	

Example 2. Fast curing cement

Solution	A	B	Prepare separate solutions A and B.
Neoprene type S.C.	100	100	Dissolve 20 parts in 80 parts benzene. Vulcanization: about 24 hours at 20° C.
Zinc oxide	10	—	
Calc. magnesia	—	10	
Pyrocatechol (accel.)	—	2	
Salicylic acid (accel.)	2	—	

Mixtures of Neoprene AC with a thermoplastic phenolic resin dissolved in toluene + methylethylketone are suitable for the bonding of cured natural and synthetic rubbers to metals and other surfaces. The application of Neoprene cements in metal bonding will be discussed below.

Nitrile rubbers³¹ are more oil-resistant than Neoprene, but lack the high tensile strength of the unpigmented film as well as tackiness. They share with Neoprene the tendency to gel prematurely. Again breaking down on the mill to produce a smooth solution in a mixture of polar solvents is a tricky job, requiring more experience and care than the handling of natural rubber. Pigmentation with special types of carbon black, clay or silene (a SiO₂-type filler) is necessary, while high-boiling solvents or plasticizers increase the tack. The dry film has sufficient strength for practical purposes. Curing requires somewhat less sulphur and more accelerator than natural rubber.

A modified natural rubber³² has been prepared by the interaction of acrylic nitrile and natural rubber in the presence of peroxides. The product (Canite) consists probably of polyacrylonitrile chains tagged to the rubber molecule by incidental reactions. The presence of nitrile groups modifies the adhesive properties of the original rubber; however, the product is somewhat unstable and it is difficult to obtain a smooth solution. Solutions

of this polymer have been proposed as adhesives in combination with chlorinated rubber, which are said to be superior to chlorinated rubber alone. Their practical value is still sub judice.

The combination of nitrile rubbers of the Perbunan and Hycar type with a second polymer is a recent development of great promise. Alcohol-soluble phenolic resins (Novolaks) are dissolved in methylethylketone, containing Hycar as a strongly swollen gel. A well-known product, Pliobond, was analyzed by the authors and found to consist of 20% nitrile rubber with 7.6% N, 10% resin and 70% solvent, but many other combinations are possible. The resin, which consists in this particular case of a phenolic polymer containing N and S, is the actual adhesive, which also cures the rubber on heating.

This new type of rubbery adhesives is useful, not only for the bonding of elastomers to other materials, but also for polymers of the PVC-type. Large quantities of plasticizers in PVC create a new problem. The plasticizer tends to migrate in the adhesive film, causing it to become soft and sticky. The resin-nitrile rubber combination is sufficiently resistant and has the additional advantage that a technique, similar to that used in rubber manufacture, can be employed.

Combinations of chlorinated rubber and nitrile rubber are also advocated for this purpose, the former being a strong adhesive for PVC but reducing somewhat the oil resistance of the joint. Another alternative is the application of vinylchloride-vinylacetate copolymers. The latter can be adapted to special purposes by changing the monomer ratio. There is no definite limit between the polyvinylacetate, the nitrocellulose and the rubber type adhesive. Economic considerations, tradition and technical details, such as drying time, are all factors influencing the ultimate choice of a suitable adhesive. Chlorinated rubber, cyclized rubber and rubber hydrochloride are essentially bonding agents for rubber to metals and will be discussed in § 5. Similar cements have been suggested for the bonding of rubber to textiles and other materials, but little is known about their actual application for such purposes. Reaction products of rubber and rubber halides with phenols have been extensively discussed in patents, but have little advantage over less intricate formulas of thermosetting or thermoplastic adhesives.

The application of polyisocyanates is not restricted to the rubber-metal and rubber-cord bond, see § 6, but has gradually been adapted to a variety of purposes, which widen the possible uses of rubber and chlorinated rubber cements. Added to a cement made up from Neoprene and chlorinated rubber, polyisocyanates improve the bonding of rubber to a variety

of materials, e.g. methacrylate resin, phenol formaldehyde resin, polyvinyl-chloride and ceramics.

Although the trend to produce "tailor-made" synthetic adhesives has led to considerable improvements, it is found that in some industries gutta-percha, a natural product, cannot be readily substituted by synthetic polymers. Mixtures of gutta-percha and asphalt combine a suitable melt viscosity with excellent adhesive properties in the cold. Gutta-percha is also used in continuous paper processing for repairing a ruptured paper sheet by bonding the two parts on the roll.

§ 5. THE ADHESION OF RUBBER TO METALS ³³

(a) *General Remarks*

Elastomers have many desirable properties, such as resistance to corrosive chemicals and to abrasion, absorption of vibration, properties which are not found to the same extent in metals. They lack, however, the rigidity frequently necessary for a construction material and are therefore combined with metals to yield a structure of the desired stiffness. Adhesion of rubber to iron and steel had already been successfully effected in the last century, but with the recent developments in the automotive and aircraft industries, the bonding of elastomers to light metals and alloys has become vital. The problem is not only that of producing a bond, but also of bridging the divergent mechanical properties. Natural rubber is unique in its versatile rheological behaviour, which can be varied between wide limits by suitable compounding. In addition, many plastics are mechanically similar to a filled rubber and are employed in the same field, e.g. for tank lining. The construction engineer is therefore faced with two problems:

(1) The design of a joint, which is intermediate in mechanical properties between a rigid metal and a plastic-elastic polymer. Thermostability, resistance to mechanical vibration, solvents and corrosive liquids, or to heat-aging are additional factors which influence his choice of bonding material or method.

(2) The economics of processing, which are not only specific for the various adhesives but depend on the type of factory, the size of the product and the amount of piece work involved in manufacturing it.

The technical question is therefore not in the first place what method leads to the best joint, but what process combines an optimum of desirable engineering and economic factors. We shall discuss first the merits of the four different methods known to be practised in industry at present ³⁴.

The use of ebonite as a bonding layer is nearly a century old^{35a}. Its application is widespread for various purposes. Both bondings of tyre treads to steel rims and protective coatings for tanks, pipes and valves can be readily prepared from ebonite, the manufacture of which is within the scope of any rubber factory. The main disadvantages of this bond are its brittleness and, therefore, sensitivity to vibration, its thermoplasticity and (on exposure to air) the deteriorating influence of a high sulphur concentration on the aging of a covering soft rubber layer.

The curious combination of latex-blood albumen and sulphur, which was formerly used to some extent, takes an intermediate position between ebonite and fluid adhesives. A more promising line is that of cements based on thermoplastic rubber derivatives, among which chlorinated rubber excels all other products previously suggested. The combinations based on nitrile rubbers are the most recent type of cement for joining rubber to metals and other materials. These adhesives are less brittle if correctly compounded and require a technique sometimes preferable to that employed in the use of ebonite. The adhesive/metal bond is, however, extremely sensitive to small flaws in the interface; moreover, the necessity of strict control and trained personnel for production militates against the adoption of the method for general use.

The third group, the isocyanates, only came into prominence during the late war. The bond is to a certain extent thermoplastic, but much more reliable than that produced by thermoplastic adhesives. A serious drawback, however, is the fact that the "pot life" of the solution is measured by hours rather than by days and that the adhesive is destroyed by traces of moisture. As the relative humidity in a rubber factory is generally high, owing to handling open steam curing apparatus, leaky valves and pipe lines, the use of isocyanate-base adhesives is a difficult proposition. Another drawback is the toxicity of adhesive and solvent. Isocyanates therefore require a highly organized and continuous production process.

The fourth method of bonding, which is known as "brass plating", was incidentally discovered at the beginning of this century and its use in specialized factories is being promoted by systematic research and the elimination of a number of intriguing complications. The rubber-to-brass bond is definitely non-thermoplastic and must therefore be chemical rather than physical in nature. It is resistant to vibration as well as to chemical attack, properties which are attractive to the construction engineer. Unfortunately, a special brass plating unit must be added to the factory, which requires additional attention and therefore increases cost of production.

The strength of the rubber-to-metal bond has already been discussed in § 2. The nature of the bonding forces is deduced from the thermoplasticity of the bond in a temperature region where the modulus of the vulcanized rubber changes but little. It can be seen from Fig. 147, which is based on

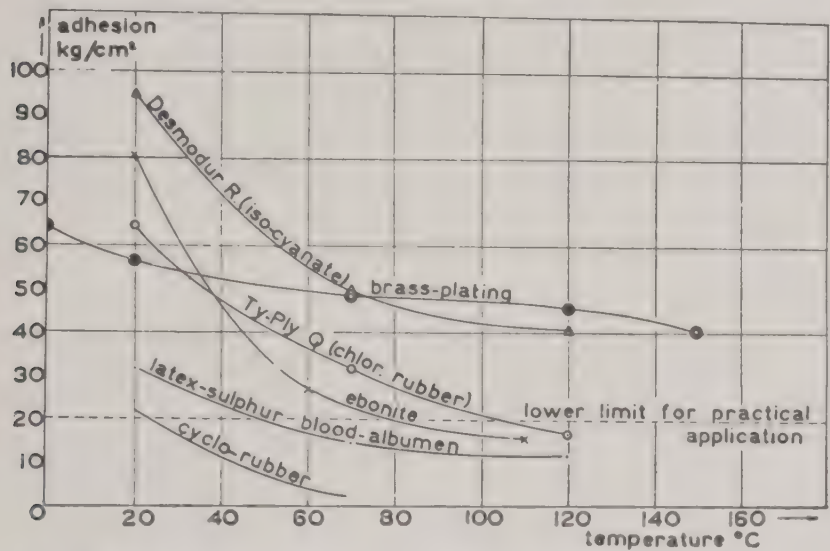


Fig. 147. Influence of temperature on the absolute value of a rubber-to-metal adhesive bond measured by the pull test and produced by different types of adhesives.
Natural rubber with 44 parts by weight of carbon black, type EPC, to steel.

measurements from this laboratory as well as on results taken from the literature, that three types of bonding exist.

- (1) The isocyanate and brass bonds are moderately thermoplastic between 0–150° C.
- (2) The ebonite and chlorinated rubber-type bonds are at 20° C superior in static strength to the brass bond at 20° C, but rapidly deteriorate in usefulness above 60–80° C.
- (3) The cyclorubber and latex-albumen-sulphur types of bond, which even at 20° C are inferior in strength to the second group and lose all practical value at a slightly higher temperature.

It is obvious, therefore, that the second and third types of bonding agent react exclusively through VAN DER WAALS' or electrostatic forces of similar strength, whereas the isocyanate and brass bond is largely a strong "chemical" bond.

Measuring the strength of a piece of rubber vulcanized between two metal plates is one thing, revealing a certain aspect, but the actual performance

of this bond in a construction unit is quite a different proposition. A good adhesive bond is useless if the design of the rubber coupling or mounting is faulty. Concentration of stresses on the rubber part by edges and corners may induce excessive fatigue or creep in the elastomer. Allowance must also be made for the contraction of rubber during vulcanization and full use of its resilience is only possible if the rubber is not enclosed to a large extent by the metal. Hard rubber adhesion requires a different design; dovetails and serrations may be useful here to limit the plastic flow of the bonding layer, but in changing to brass plating the construction of metal parts, for the same application, must be changed to smooth surfaces, which can be readily cleaned and plated.

(b) *Ebonite*

Ebonite is a useful lining material for tanks and bonding it to large metal surfaces has been developed to a fine art. Apart from this specific purpose, it is used for bonding soft rubber to metal, the technical problem in this case being the adjustment of vulcanization rates for soft and hard rubber.

A mixture of raw rubber with sulphur becomes soft and sticky on heating and therefore flows readily into all the microscopic crevices of a metal surface. On prolonged curing with 15–45 parts of sulphur it becomes hard and remains physically attached to the surface. During the cure, gases (H_2S) are evolved and produce bubbles in the structure. Part of the ebonite is therefore replaced by ebonite dust, which also reduces the evolution of internal heat during cure (see Table 61). Shrinkage on cooling and a coefficient of expansion differing from that of the metal weaken the bond^{35b}. The resulting formation of cavities on the interface can be kept within bounds by the addition of fillers. The nature of the filler is of little importance, its average function being that of reducing shrinkage.

The adhesive bond to iron was found in this laboratory for an unfilled ebonite to spread between 10–20 kg/cm², while on the addition of 24 parts by volume of barytes, whiting or ebonite dust, the bond produced had an average strength of 60 kg/cm² (40–90). Iron oxide (24 parts by volume) is somewhat superior, the resulting bond surpassing 100 kg/cm² (90–120). The claim that mixtures of iron oxide and whiting give optimum values³⁶ has not been substantiated by experiments (taking the reproducibility of the test into account). It is seen from Table 61 that the bonding strength of the filled ebonites varies between 50–100 kg/cm² in the static tests. An unfilled ebonite, on the other hand, is useless for this purpose, although the latter material, measured by itself, has a very high impact strength (100 kg/cm²).

TABLE 61

COMPOSITION AND PROPERTIES OF EBONITES USED FOR BONDING RUBBER TO METAL
(quantities in parts by weight)

Mix No.	1	2	3	4	5	6a *	6b **
Rubber	100	100	100	100	100	100	100
Sulphur	40	40	40	40	40	27	18
Zinc oxide	5	5	5	5	5	4	—
Barytes	—	105	—	—	—	220	—
Ebonite dust	—	—	27	—	—	—	—
Whiting	—	—	—	65	—	—	—
Iron oxide	—	—	—	—	130	—	—
Kaolin	—	—	—	—	—	—	47
Stearic acid	1	1	1	1	1	—	—
Santocure	3	3	3	3	3	—	—
Antioxidant	—	—	—	—	—	—	2
Vulc. time min. at 147° C	120	100	100	100	100	180	180
Pressure on test piece during vulc. kg/cm ²	0.02	0.02	0.02	0.02	0.02	0.1	0.1
Shore C Durometer hardness	92	92	92	92	92	45	85
Adhesion to steel kg/cm ²	12	52	64	73	106	81	

* Solution mix; ** Lining mix. For mixtures 1-5, solution and lining mix are the same.

Vulcanization can be accelerated, but depends much on the heat transfer and the total curing time; it may extend to days. For tank lining the uncured mix is rolled on the surface of the metal, the tank filled with hot water and cured by blowing steam through it. Hot air or steam cures are alternatives.

From a mechanical point of view, it would be desirable to combine soft rubber and metals by a number of laminae with increasing sulphur concentrations. In practice one has to find the balance between two sources of weakness, *viz.*,

(1) The curing time of ebonite is much longer than that of the rubber. The latter will therefore be over-vulcanized and will have bad ageing properties when the former is fully cured.

(2) Under-curing the ebonite leads to a surplus of free sulphur. Gradually this sulphur will diffuse into the intermediate or even the outer layer of soft rubber and will again induce oxidation. This is less likely to happen in structures in which the adhesive layer is not accessible to air.

Ebonite can be bonded to most metals including tin, zinc and chromium³⁷. Copper and certain brasses react with the sulphur and have to be passivated by tinning or similar treatment. Aluminum is cleansed first with dilute hydrochloric acid solution and care must be taken not to damage the

clean and dry surface before applying the adhesive. Rust and scale must, of course, be removed from iron or steel surfaces by means of wire brushing, sand or shot-blasting. After moistening the surface with petrol, one or two ebonite cement layers are applied before affixing the rubber-sulphur mix.

The butadiene-base synthetic rubbers of the G.R.S. or nitrile type undergo a similar reaction with sulphur and the resulting product differs from the natural derivatives in details only. They have a higher softening point, which is attractive for uses at higher temperature and the nitrile rubbers are "oil resistant". When vulcanizing a Neoprene mix containing 30 parts of sulphur per 100 Neoprene for 8h/142° C, a product similar to natural rubber ebonite has been obtained in this laboratory, but the properties are inferior. Neoprene "ebonite" has found no application as an adhesive or protecting layer. Mixtures of Neoprene and natural rubber with about 15 parts of sulphur relative to the polymers are used as suitable bonding plies.

The application of latex-ebonite as an adhesive has not been fully explored, but unpublished results from this laboratory are promising. Its use is a logical consequence following from the adhesive properties of latex-sulphur-albumen mixes.

(c) *Thermoplastic Adhesives*

It is not difficult to compound a cement suitable for the bonding of one particular rubber mix to only one type of metal surface. The secret of most proprietary cements is that they can be used for bonding a fairly large range of combinations. Several alternatives are known. The first cement to be discussed now shares with other latex adhesives the advantage of being non-inflammable and giving a bond of moderate strength. The second group, adhesives derived from chlorinated rubber, is the most promising for future development, while the third group, comprising cyclized rubbers, is more of historical interest.

(i) *Adhesives based on latex-albumen-sulphur mixes* ³⁸

The idea of combining the adhesive and mechanical properties of rubber and proteins by mixing blood albumen and latex did not lead immediately to practical results. It was found that 18–40 parts of sulphur had to be added; thus, under the conditions of vulcanization, a semi-ebonite will be formed. The process is, however, more intricate, oxidation playing some part in it. When the latex-blood albumen layer is applied to the metal, the

assembly, after drying 1 h/70° C, has to be heated for 2 h/120° C in air before the rubber is vulcanized to the adhesive layer. Heating in nitrogen gives a very poor bond.

A composition proposed by FLINT³⁹ was found also in this laboratory to yield optimum values. It consists of 100 parts of rubber as latex, 140 parts albumen, 18 parts sulphur, zinc oxide and not more than 1 part D.P.G. A layer of 2–3 mm is brushed on the metal and, after drying at 70° and oxidizing at 120° C, a rather irregular adhesive film with a thickness varying between 0.6–1.3 mm results. Neither sulphur and accelerator concentration, nor the thickness of the film is very critical. The latter fact marks a striking difference compared with the chlorinated rubber base adhesives, in which the thickness of the film is found to be of the utmost importance. The strength of the adhesive bond is less than that of chlorinated rubber, about 12–25 kg/cm², depending on the composition. Starting from this lower limit, the percentage drop in adhesive strength at higher temperatures is apparently small; see Fig. 147. The adhesive adheres well to the metal and separation occurs primarily between the rubber and the adhesive. The mixture has only limited shelf life; it will begin to putrefy after some weeks, even in the presence of formaldehyde. Its main advantages are cheapness and simplicity of procedure.

The method can be applied to butadiene-based rubbers but not to Neoprene. Loaded natural rubber stocks produced better results than pure gum mixes. Steel as well as aluminum can be bonded to rubber, if the surface treatment of the metal discussed previously has been applied.

(ii) *Chlorine-containing polymers*

Films from chlorinated rubber are chemically inert; they exhibit excellent resistance to normal and accelerated aging and do not absorb water to any appreciable extent. The metal-chlorinated rubber bond does not deteriorate under salt spray treatment and is in this respect to be preferred to the brass bond. The polar polymer is readily miscible with Neoprene and the bonding of this elastomer to metals and other surfaces with chlorinated rubber is comparatively simple^{40, 41}. As the film is rather brittle, either Neoprene or a softener is added to improve its flexibility. Two or three layers of the adhesive are painted on the metal and the Neoprene rubber is pressed on it before the last layer is dry (the solvent can diffuse through the elastomer). The cements are made up of xylene; red lead or sulphur is recommended as an ingredient. The application of a Neoprene interlayer with a Shore hardness of 50–70° is more satisfactory in some instances. Vulcanized Neoprene can be bonded with similar cements.

The affinity of chlorinated rubber for nitrile rubbers is also satisfactory, but a somewhat more complicated technique has to be followed⁴². A chlorinated rubber cement is painted on the metal and a vulcanizing nitrile rubber cement is brushed over the first lacquer as well as on the rubber surface. This is followed by conventional vulcanization of the joined parts.

Natural rubber is not fully miscible with chlorinated rubber and for this reason separation of the rubber-to-adhesive bond may occur. The thickness of the lacquer layer is therefore more critical than with polar elastomers. Though adhesive solutions are mostly made up in the factory from ordinary chlorinated rubber, proprietary adhesives have recently had some publicity⁴³. The "Typly" solutions are said to contain rubber hydrochloride, but the latest type, "Typly Q", was analyzed by the authors and found to consist of a solution of chlorinated rubber (22% with a chlorine content of 61%) dissolved in a mixture of xylene and carbon tetrachloride (3:2). This solution has a limited shelf life; the polymer or admixtures tend to precipitate, which makes its use in the factory inconvenient.

Reproducibility of bonding with "Typly Q" was extensively studied in this laboratory. An average value of 50 kg/cm² (40–80 kg/cm²) was found to be fairly independent of (1) the plasticity of the rubber-carbon black mix, (2) sulphur concentration, (3) rate and method of vulcanization, (4) rate of cooling after vulcanization and (5) aging of the joint at 40° C. Only a slight improvement was found by the application of high pressure (160 kg/cm²) during vulcanization. The drying time for the paint-on-metal layer

is rather critical. A short time at 70° C gave better results than 24 hours storing (dust free) at 20° C. Some improvement was also obtained by coating the chlorinated rubber layer with a rubber solution.

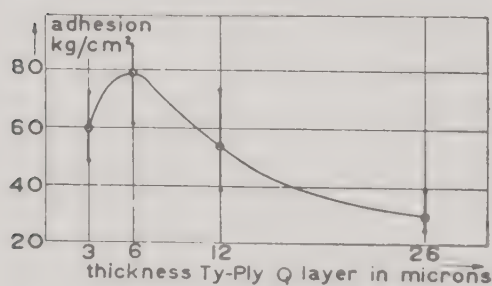


Fig. 148. Influence of thickness of adhesive layer on strength of adhesive bond.

Pull test with chlorinated rubber adhesive, see Figure 144, p. 395. Natural rubber with 44 parts by weight of carbon black, type EPC, to steel.

15 microns; whereas break occurs between rubber and the thin lacquer layer, those 25 microns thick break in the film, which is actually microporous.

This sensitivity to the thickness of the layer has been a serious handicap

in processing with chlorinated rubbers. Combination with other polymers, of which the isocyanates are the most promising, will lead to further improvement. Little is yet known about the use of other chlorine-containing polymers in rubber-to-metal adhesives. The particular position of chlorinated rubber is probably due to the fact that small quantities of hydrochloric acid are released during vulcanization and remove part of the oxide film on the metal. Similar properties are found in chlorinated polyvinylchloride, which is preferred for the bonding of rigid polyvinylchloride to steel and could probably be substituted for chlorinated rubber in other cases.

Polyethene and butyl rubber cannot be bonded with polar adhesives. Quite recently ^{41b} it has been reported that chlorination of the surface of polyethene imparts good bonding properties to this polymer.

(iii) *Cyclized rubber adhesives* ⁴⁴⁻⁴⁹

Cyclized rubber can be either produced on the surface of the rubber or applied as a cement. In the first case the surface of the raw rubber mix is treated with sulphuric acid and vulcanized on the steel. The authors do not believe that this "Vulcalock" process has gained much ground. Recently the "cycleweld" process has been disclosed. In this case vulcanized rubber is cyclized superficially by the action of concentrated sulphuric acid, washed and dried. It is then flexed to produce a finely cracked surface. "Chrysler cement", probably a nitrile rubber-resin composition, is sprayed or brushed on rubber and metal. The good bonding properties are in this case due to the cement and the cyclorubber surface has only the function of producing a smooth change in mechanical properties. This "cycleweld" process can also be used for bonding rubber to wood, glass, plastics and elastomers.

Cyclized rubber solutions are very sticky, but produce only a weak rubber-to-metal bond. Values of 34 kg/cm² are claimed from the laboratory of the manufacturers of "Vulcabond R", but in this laboratory average values of 10-17 kg/cm² (7-18) were found under optimum conditions. Not only is vulcanization under pressure necessary, but the mould has to be cooled under pressure, otherwise values below 5 kg/cm² will be found for the adhesive bond. The cement is applied as follows:

A layer of cyclized rubber is applied to the metal surface (*e.g.*, steel or aluminum) by brushing or spraying two coats of a cement. The dry surfaces of the coated metal and the rubber mix should be safeguarded from dusting powder or other solid impurities. They are then brought together and vulcanized under pressure. The concentration of the cement and the degree of cyclization of the derivative are factors influencing the strength of the bond. The plasticity of the adhesive layer can be increased by the addition

of rubber to the solution, or by plasticizers. Fillers and vulcanizing agents are added to the cement and the adhesive film will therefore vulcanize together with the rubber. Certain ingredients which are conventional parts of rubber compounding, such as stearic acid, are detrimental to the quality of the adhesive film. Many attempts have been made to reduce the thermoplasticity of the layer by the addition of fillers, such as short-fibred asbestos, wood-flour, casein or Neoprene-rubber, but they all debase the already only moderate adhesive quality of the film. In the view of the authors, "thermoprene" cements will be replaced in future by adhesives of the nitrile rubber-resin type.

(d) *Isocyanates* ^{50, 51}

Two methods of applying isocyanates in rubber-to-metal bonding have been given attention. In the original German process, "Desmodur R" is incorporated as a 20% solution in methylene chloride, while the British manufacturers advise the use of "Vulcabond T X" as an auxiliary means of improving cementation with chlorinated rubber, rather than as an independent method of joining rubber to metals.

The "Desmodur R" cements adhere much better to roughened metal parts than to smooth surfaces. The available bonding area can be increased by shot-blasting the surface or by etching it with acids. Average bond strength values are similar to those obtained with Neoprene cement + chlorinated rubber + Vulcabond T X, but somewhat inferior to those obtained with the latter lacquer plus an interply. The heat resistance of the Desmodur bond seems to be inferior to that of the laminated Vulcabond T X joint.

The cause of isocyanate bonding is not definitely known. O. BAYER and his colleagues, who are the discoverers of the process, suggest two hypotheses: (1) The isocyanate groups react with the metal oxide layers, thus providing a strong bond with the metal surface; (2) the isocyanates polymerize and form a network mutually linking the metal, the adhesive film and the rubber.

The practical value of isocyanates of the "Desmodur R" type was proved during the late war by the fact that the German Navy replaced brass-plating (Schwingmetall) by Desmodur bonding for all rubber-metal parts in submarines. This illustrates the excellent vibration resistance of the isocyanate bond. In submarines, the brass bond is attacked by sulphuric acid fumes which do not weaken the isocyanate bond. The competition between the two processes under the conditions of peace time economy seems to be still sub judice.

The following data have been published by the manufacturers of Vulcabond T X on chlorinated rubber isocyanate combinations. To 100 parts of a cement made up of Neoprene GN and chlorinated rubber solutions in aromatic hydrocarbons, 15 parts of Vulcabond T X were added. Two coats of this adhesive were painted on the metal and left to dry. An interply of the rubber stock was then applied as a cement and finally the rubber (or Neoprene) reinforced stock added. The laboratory tests gave the following promising results:

Cement	Interply	Tensile strength kg/cm ²
Neoprene + chlor. rubber	Yes	18—23
As above + Vulcabond T X	Yes	50—100
As above	No	28—50

Although chlorinated rubber is the weakest link in this chain of interplies, its adhesive strength is improved by the treatment with isocyanates. It is likely, therefore, that a chemical interaction between the chlorinated rubber and the isocyanate also takes place. The efficiency of chlorinated rubber cement, which is in itself good enough for many purposes, is improved twofold by the addition of the isocyanate and fourfold in a combination with an interply. The latter contributes towards improving the bond between rubber and chlorinated rubber, while the isocyanate strengthens not only the adhesive film, but also its thermostability. A test at 100° C in air and even in boiling water yielded a strength of 40–45 kg/cm², with the break occurring in the rubber. From the point of view of tensile strength, the new adhesive combination certainly produces promising values for a non-brass bond. Further data on the vibration resistance of this chlorinated rubber-isocyanate joint will have to be awaited before its ultimate industrial value can be established.

(e) *Brass Plating*^{52, 53}

Not all the sulphur reacting with the hydrocarbon in a soft rubber mix is used instantaneously for cross-linking. Arguments can be put forward for the formation of –SH groups, which will have a strong affinity for metallic copper and act as an “adhesive”. A number of such sulphur links between the rubber and the copper is sufficient to produce strong chemical bonding. Reasoning from analogy with cross-linking reactions, about one sulphur-bridge to 100 isoprene units of the rubber should be sufficient. Copper,

on the other hand, reacts vigorously with sulphur and the rapid formation of a copper sulphide layer precedes vulcanization and bonding reactions. The secret of the brass layer then is the dilution and passivation of the copper surface. This complex problem has been clarified by a number of fascinating experiments performed by BUCHAN.

After rigorous cleaning and de-greasing, most metal surfaces can be brass-plated, but only a specific type of plating is suitable for bonding rubber. For details the reader is referred to BUCHAN's work, the following points of general interest being taken from his monograph.

The plating plant should have facilities for hand-operated plating, automatic plating, barrel plating of very small units and special pre-treatment of alloys. Attention must be given to the correct composition of the electroplating solution as well as to the cleaning bath. Pores and non-homogeneous surfaces of the metal lead to bad bonding, even if the plating is correctly done. Apparently identical brass surfaces showed considerable differences in bonding capacity. Examination of the surface by electron-micrographs and electron-diffraction technique revealed the co-deposition of foreign substance with the brass or non-uniform deposit as the ultimate cause of bond failure. One of the less obvious potential sources of failure is the co-deposition of complexes of the type $(\text{Zn}(\text{NH}_3)_6)$ $(\text{Zn}_3(\text{Fe}(\text{CN})_6)_2)$. The deposition of such complexes depends on the composition of the bath. It explains why a bath has to be used sometimes for some hours before satisfactory brass surfaces can be obtained. Processing control includes current density, metallic salt concentration, pH, temperature and the addition of ammonia. The latter acts as current carrier counterbalancing cathodic polarisation.

The formation of a good rubber-to-brass bond depends on the correct balance between the two processes:

$$\frac{\text{rate of reaction of sulphur with brass}}{\text{rate of reaction of sulphur with rubber}}$$

A rapid reaction of sulphur with brass will lead to the formation of copper sulphide, preventing bonding with rubber. The reactivity of the brass depends on the method of plating; it cannot be expressed in absolute units and for this reason vulcanizing mixtures cannot be divided into good and bad ones. Some sources of bad bonding have, however, been eliminated by empirical work. Fast accelerating, scorchy mixes should be avoided. Moderate retardation during processing and at the beginning of the cure appears to be an advantage. Accelerators of the M.B.T. type are preferred; the accelerator/sulphur ratio seems sometimes to be more critical for bond strength than for optimum rubber cure. Certain accelerators of the T.M.T.

type lead to sulphide formation on the brass, preventing an adhesive bond. Buchan suggests the use of thioplast layers as an alternative source of reactive sulphur.

The composition of the rubber mix obviously depends on the ultimate use of the product. Sometimes it is possible to extrude the rubber on to the brass surface and vulcanize in suitable moulds; in other cases it is necessary to deposit on the brass surface a bonding cement, differing in composition from the rubber body.

A bonding cement from natural rubber is also a useful aid towards improving the inferior adhesion obtained with G.R.S. and Buna S. No difficulty seems to be experienced in bonding nitrile rubbers to brass. Although Neoprene is vulcanized without sulphur, the latter is an essential ingredient in bonding the various types of Neoprene to brass. Excellent bonds between butyl rubber and brass can be obtained if (1) the compound is stiffened by the addition of clay and, (2) very high concentrations of accelerators of the thiuram type are used to speed up vulcanization. Although these accelerators prevent bonding of natural rubber mixes by reaction with the brass, they have a beneficial effect on the bonding of butyl rubber, which has only a few double bonds and therefore slow vulcanizing characteristics.

It appears that any polymer capable of reacting with sulphur can be bonded during the vulcanization process to brass. Sulphur reacts with many other metals and it is to be expected that this method of adhesion will be applied to other rubber-metal combinations. Although several metals e.g. nickel, aluminum, bronze and phosphor bronze are occasionally mentioned as giving good adhesion with rubber on vulcanization, none of them has been applied on a large scale. The production of another metal surface with reproducible reactivity towards rubber-sulphur mixes could only be achieved by carefully planned research.

§ 6. THE ADHESION OF RUBBER TO FIBRES

(a) *General Remarks*

Strong adhesion of rubber to cotton is produced by vulcanization alone in the absence of any special adhesive. Fabrics are frequently proofed by cold curing with sulphur chloride solutions, which seem to produce a "handle" difficult to obtain with other vulcanizing agents. Gasoline or benzene are mostly used as a solvent, but carbon disulphide is still employed for special purposes. Attempts are now being made to replace it by mixtures of less objectionable solvents.

The appearance of rayon and nylon has raised many new problems of adhesion, which have been extensively studied in tyre-cord production, and will be discussed now. The last section gives some particulars on adhesive tape processing.

(b) *Rubber-Cord Adhesion* ⁵⁴⁻⁵⁸

Rayon is everywhere ousting cotton in tyre cord. The strength of the former does not deteriorate to the same extent as cotton at 95–120° C, a property particularly valuable in G.R.S. tyres, which develop higher temperatures than natural rubber. It was found at first that the adhesion of natural or synthetic rubber films to rayon was very weak. To-day we know from the systematic study of fabrics that these differences are essentially due to different fibre surfaces. The fine hairs of cotton create a large surface, which is mechanically interlinked with the rubber and contributes to the adhesive bond. Continuous filament viscose, acetate rayon and nylon lack these structural irregularities, whereas fabrics woven from spun staple fibres regain a fraction of the cotton quality, this being probably due to the protruding ends of the staple fibres. Another factor influencing the adhesive bond is the extensibility of the fibre. Special high tenacity rayon has to be used. Adhesion between rubber and rayon is enhanced by special adhesives. Three distinct classes are known at present:

- (1) Impregnation with a vulcanizing latex-borax-casein mixture, or even a reclaim emulsion-latex-casein mix omitting vulcanizing ingredients. The latter will diffuse from the rubber body into the bonding layer during vulcanization.
- (2) Impregnation with a latex-resorcinol-formaldehyde mix. Here the resin possibly acts as a cross-linking agent.
- (3) Impregnation with an isocyanate solution.

Table 62 gives some relative figures ⁵⁹ which illustrate, not only the value of the bonding method, but also the significance of dynamic testing. It is seen that the static strength of the cotton-rubber bond is only twice that of rayon, whereas the dynamic fatigue life is twenty times longer. Isocyanate bonding improves the dynamic fatigue of the rayon cord by a factor of 75–165, while the static test would give the impression of a much smaller improvement. Isocyanates make the rayon bond equal or superior to the untreated cotton-natural rubber bond.

Results for nylon are similar as far as adhesion and fatigue resistance are concerned, but the fabric has the disadvantage of excessive growth in service. Finally, it should be mentioned that steel wire cords are used

TABLE 62

STATIC AND DYNAMIC FATIGUE OF RUBBER—CORD ADHESION AT 80° C
(after FROMANDI (59))

Dynamic test: 2 cm of cord are vulcanized into a carcass mixture. The test piece is moved to and fro at a rate of 500 cycl./min. Unit: rupture after X minutes.
Static test: Unit: kg/cm².

A. Influence of rubber and cord material on the adhesive bond
No impregnation of the cord

Cord material	Cotton		Rayon		<div>Cotton Rayon</div>	
Test method	Static kg/cm²	Dynamic min.	Static kg/cm²	Dynamic min.	Static	Dynamic
Natural rubber	5.6	55	2.8	3	2.0	18
Buna S 3	4.1	20	1.8	1	2.3	20

B. Influence of impregnation on adhesion of rubber to rayon
Cord material rayon

Polymer	Natural rubber		Buna S 3	
Test method	Static kg/cm²	Dynamic min.	Static kg/cm²	Dynamic min.
Desmodur R impregnation	9.1	250	7.2	165
Latex-resorcinol resin imp.	4.8	65	4.2	45
No impregnation	2.8	3	1.8	1
Improvement by Desmodur. Factor:	3.3	75	4.0	165

where operating conditions are particularly severe, in which event adhesion raises no special problems.

Isocyanate bonding does not measurably improve the adhesion of rubber to cotton fabric or duck when measured in a static peeling test. The flex life of a laminated fabric treated with 10% Desmodur R is, however, increased from 2 min. to about 17 min. An isocyanate treatment will therefore reduce the number of failures due to separation of the cotton and the rubber.

(c) *Adhesive Tape*

In frictioning an adhesive layer upon a continuous backing of cotton, cellophane or another plastic film, adjustment of temperature is the decisive factor. The adhesive has to be sufficiently sticky to adhere to the tape, but must stick neither to the third roll nor to the back of the next layer when wound up. The adhesive is therefore fed to a three-roll calender, the middle

roll being kept at a moderate temperature. An alternative method is spraying the adhesive from a solution.

The classical surgical plaster mass consisted of lead oleate mixed with resins. It had, however, to be warmed before application and was decomposed by secretions of the skin. The introduction of a rubber component therefore marked considerable progress. Colophony is added to increase the tack, but it causes peroxide formation and the rubber is quickly hardened and destroyed upon exposure to air and light. W.W. (water white) colophony is less likely to cause skin irritation and is therefore preferred. Liquid paraffin is added to prevent drying up and another component is linseed oil or wool grease to soothe the skin. Zinc oxide and other fillers are added. The rubber (20–40 parts) in this case acts as a strong macromolecular backbone to the sticky paste. For use in tropical countries a higher rubber and lower oil content is necessary in order to avoid excessive stickiness. A close-woven fabric from plain bleached cotton has to be used to prevent the paste from seeping through.

The introduction of an elastic plaster was a great improvement in surgical technique. Elasticity is due partly to the use of crepe yarns for the warp or weft of the base cloth and partly to the elasticity of the rubber-adhesive compound itself, which is preferably processed from a solvent.

Pressure-sensitive tapes are made from 100 parts of well broken-down rubber with 140–180 parts of a resin and 75–125 parts of zinc oxide. Transparency can be obtained by using a low acid type ester gum in a volatile solvent and the omission of mineral fillers.

The mass of an industrial tape is essentially the same as for a surgical plaster, but there is a greater variety of suitable basic materials. Insulating tape must contain no ingredients which would corrode copper wire; its colophony content is therefore lower so as to minimize acidity.

§ 7. LITERATURE, REFERENCES AND PATENTS

(a) *Books on Rubber, Rubber derivatives and Rubber adhesives*

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U.S. = number of American Patents

G.B. = number of British Patents

*Group 1 : Latex adhesives
based on natural rubber*

U.S.	2,247,293	2,320,937
	2,256,153	2,335,104
	2,302,378	2,357,676
	2,302,387	2,371,899
	2,310,972	2,411,905
	2,311,301	2,417,975
	2,318,126	

G.B.	542,331	572,232
	561,491	575,767

based on synthetic rubber

U.S.	2,419,816
G.B.	578,304

*Group 2 : Adhesive solutions
based on natural rubber*

U.S.	2,181,538	2,278,802	2,364,847
	2,188,283	2,278,943	2,375,162
	2,188,331	2,279,256	2,375,163
	2,203,677	2,295,866	2,377,647
	2,229,317	2,297,871	2,382,731
	2,236,527	2,304,678	2,397,627
	2,236,567	2,307,801	2,410,078
	2,251,220	2,325,562	2,412,182
	2,254,321	2,338,948	2,416,925
			2,424,736
G.B.	549,885	570,175	
	556,147	575,767	
	562,987	580,333	
	570,173	585,859	

based on synthetic rubber

U.S.	2,227,900	2,398,108
	2,392,590	2,400,474
	2,393,495	2,417,792
	2,395,070	2,423,755

G.B.	580,190	585,859
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based on rubber derivatives

U.S.	2,218,617	2,281,087	2,398,735
	2,236,597	2,311,656	2,407,143
	2,259,190	2,373,308	2,410,053
	2,259,331	2,375,163	2,413,432
			2,425,348
G.B.	546,636	578,019	
	549,977	579,447	585,060
	557,162	581,137	585,664

based on mixtures of rubbers and resins

U.S.	2,290,205	2,364,847	2,381,186
	2,352,637	2,366,219	2,392,618
	2,352,705	2,376,777/8	2,418,025
			2,424,736
G.B.	595,290		

Group 3: Metal plating

U.S.	2,240,805	2,399,019
	2,240,862	2,409,759
G.B.	577,702	

CHAPTER 8

ADHESION IN SOLDERED JOINTS

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§ 1. INTRODUCTORY

A soldered joint is made by introducing molten solder, an alloy of tin and lead in variable proportions, between specially prepared and heated metal surfaces and then allowing it to cool. Another method, which is much used, begins by forming a coating of solder, or of pure tin, upon the surfaces in a preliminary operation known as tinning, and then bringing the two surfaces together while heating them sufficiently to melt the coatings so that these flow and merge together as in a welding operation; cooling then effects joining into a solid assembly. The advantage, as compared with welding, is that the joining is done at a temperature far below the melting points of the metals being joined, and there is, consequently, no risk of damaging or destroying the shape of the articles; for example, soldering is usually carried out at temperatures of about 300°C on metals such as brass and steel which melt at 1000°C or higher; when it is necessary to solder more easily melted metals, such as pewter or plain lead, it is the usual practice to use a solder of specially low melting point, for example, the bismuth alloy 43 per cent. tin, 57 per cent. bismuth, having a melting point of 132°C , or Wood's alloy which melts at only 70°C ³⁰.

§ 2. SOLDERING CONTRASTED WITH GLUING

The principle of making soldered joints rests on the ability of molten solder or tin to flow over solid metals and cling tenaciously to them after cooling and solidifying. There are certain similarities of a superficial kind between soldered and glued joints, but also some very obvious differences. In both types of joint, the adhesive medium during the making of the joint is fluid and flows freely upon the surfaces and fills the spaces between them, and then at a later stage, adhesion develops. In both glued and soldered joints, too, it is usually possible to coat the joining surfaces separately, and

at different times, and to effect joining between the coated surfaces at some later time. In all glues, solidification in the joint may result from reduction of the amount of water or solvent contained in them as a result of drying in the atmosphere or by absorption into the material adjacent to the joint, or by polymerisation into molecules of much higher viscosity. In solders, viscosity in the liquid state is always too low and inadequate to serve as the bonding agency; so long as the solder is molten there is no anchorage between the two surfaces; change of state from liquid to solid, as a result of temperature fall, is essential.

§ 3. INFLUENCE OF SURFACE CONDITION

The pouring of molten solder between two closely adjacent surfaces of metal, such as steel, results, after cooling has occurred, in the forming of a thin slab of solder between those surfaces. Usually, the application of quite a small force, generally a few pounds per square inch of the contact areas, suffices to pull away the steel from the slab of solder leaving them as free of solder as they were originally. By contrast, when the pouring of the solder between the two pieces of steel follows a suitable pre-treatment of the steel surfaces, the slab of solder is found to be strongly adherent and a force of some tons per square inch is needed in order to separate the two pieces of steel; moreover, the separation from the solder is not complete for the layer, or slab, of solder is pulled apart and some of the solder adheres to both steel surfaces. The forces of cohesion within the slab of solder in these two instances are the same but there is a notable difference in the degree of adhesion to the enclosing steel plates. This strong adhesion of the solder is the essence of soldering which, by its derivation means to make solid.

§ 4. COHESION AND ADHESION IN SOLDERED JOINTS

When the attempt is made to pull apart a pair of soldered surfaces, A and B, the force is applied against the adhesion of the solder to each metal surface and against the cohesion within the solid metals and in the solder. The chain of resisting forces is:

- (1) cohesion in metal A;
- (2) adhesion of metal A to solder;
- (3) cohesion in the solder;
- (4) adhesion of solder to the metal B;
- (5) cohesion in metal B.

The value of the cohesive forces (1) and (5) is not in question but it is necessary to note that, usually, they are greater than (2), (3) and (4) as shown by the eventual fracture of the joint, when the applied pull is increased sufficiently, either in the solder layer (3) or at one of the solder/metal interfaces, (2) or (4), whichever of them is weakest.

(a) *Action of Flux in Soldering*

The special pre-treatment of steel or other metal surfaces which is necessary in order to bring about adhesion to the solder, consists in the cleaning of the surfaces, the coating of them with flux and the heating of them above the melting point of the solder ²¹.

(i) *Covering Action*

The cleaning treatments have the effect of removing dirt and oxide coatings from the surface. Abrasion, washing with solvents or alkalis, and pickling in acids, are the ordinary practical means of obtaining a thoroughly clean "solderable" surface. Immediately after cleaning, in order to prevent re-oxidation, the soldering flux is applied, generally while the surface of the solid metal is cold, although it is not necessary that it should be. It is sufficient that at this stage the flux should act as a cover ³ over the solid metal surface and exclude the air which would cause oxidation. Steel, copper, brass and some other metals do not oxidise appreciably when coated with either tallow, stearine, palm oil, resin dissolved in alcohol, or with aqueous solutions of certain acidic metal chlorides and bromides. In contrast, aluminium forms a substantial film of oxide in the instant that a new surface of this metal is formed, whether in air or in contact with moisture or other oxygen containing substance. Petroleum jelly is also able to afford some protection against oxidation. The protection against oxidation becomes more necessary as the solid metal is gradually heated up to the soldering temperature, usually between 250 to 350° C, and it is important, therefore, that fluxes should not disappear, *e.g.*, by evaporation, decomposition or ignition, either before or during the spreading of the molten solder over the surface. Petroleum jelly readily takes fire so it is not a good cover; resin-in-alcohol flux is readily ignited at high soldering temperatures but is satisfactory below 300° C.

(ii) *Removal of Oxide*

Prevention of oxidation by virtue of ability to exclude air is one function of a soldering flux but there are several others. A second function is ability,

near the soldering temperature, to react with and remove any metallic oxide which may not have been removed by preliminary cleaning treatments or which may have formed subsequently. Substances which can be used as soldering fluxes are either acids or compounds which, at soldering temperatures, decompose into acidic substances with corrosive action on the solderable metals. Tallow, stearine and palm oil, just mentioned, are glycerides of fatty acids; resin breaks down into acids such as abietic acid; organic hydrochlorides, usually amine hydrochlorides, decompose with liberation of hydrochloric acid; aqueous solutions of the chlorides of zinc and tin are, in part, hydrolysed; ammonium chloride dissociates into the free acid and ammonia; phosphoric and lactic acids are active fluxes. It is noteworthy that oxidising acids and their salts have no fluxing properties for solder. For example, zinc nitrate and sulphate, and ammonium nitrate and sulphate, are not able to act as fluxes in soldering.

(iii) *Flux as a Vehicle for Reaction Products*

Although hydrochloric acid has a very strong reaction with iron and other metals it is not by itself a good flux except when by its action on the metal it produces a chloride which has fluxing properties. The reason appears to be that the acid lacks the third requisite of a flux, namely the ability to remain fluid during soldering and to act as a vehicle for the removal of the products of its reaction with both the oxide and the metal itself. When these products are not removed they form an effective barrier between the metal surface and the solder.

(iv) *Ease of Displacement by Solder*

It is essential that the adhesion of the flux to the surface being soldered should be weaker than that between the metal and the solder if the latter is to spread upon the surface.

(v) *Electrolytic Action of Flux*

There is evidence ¹⁹ that the flux acts as the electrolyte of a galvanic cell in which tin in the solder is anodic and the metal being soldered is the cathode; the tin dissolves in the flux and is thrown out of solution by contact with the bare metal acting as a cathode. The tin was visible as a halo of tin-copper compounds just ahead of the advancing meniscus of solder, according to Latin.

(vi) *Surface Tension Effects*

Flux displaces air from the solder surface where the surface tension² is about 600 dynes per cm and the interfacial tension between flux and molten solder is only about half of this value³. The lowering of the surface tension of the molten solder by the flux results in its surface increasing, that is, the solder spreads outwards under gravitational and other forces to a new position of balance or equilibrium; this would happen even if the solder were on a plate of glass instead of metal.

(vii) *Common Fluxes*

The flux most commonly employed in soldering is zinc chloride, but resin (rosin, colophony) is also much used. Other fluxes less generally used include stannous chloride, animal and vegetable tallow, palm oil, oleic acid, and phosphoric acid²¹. All these substances are liquids at soldering temperatures and are mobile on the soldered surfaces and can therefore comply with the third requirement for a soldering flux. Two substances having fluxing action but which do not undergo fusion are ammonium chloride and lactic acid; ammonium chloride is volatile and dissociates on heating; by itself it has a very inferior fluxing action.

Zinc chloride flux is commonly applied as a solution of about 30 per cent. in water with sufficient free hydrochloric acid to prevent precipitation of the basic (hydroxy) chloride, $\text{Zn}(\text{OH})\text{Cl}$. While the surface heats up to soldering temperature, most of the water boils off, leaving a crystalline hydrated chloride which melts at about 260°C . It follows that below this temperature the flux is present on the surface not as a fluid but as crystals which have no mobility²³ and therefore obstruct the spreading of the solder instead of aiding it; these unmelted crystals, if small enough, may be bridged over by the molten solder and so, by their presence, prevent adhesion at these spots. A practical solution of this difficulty is to add some ammonium chloride to the zinc chloride so as to produce the eutectic mixture of these salts with a melting point of only 170°C , which is well below the temperature at which solders are usually applied.

(b) *Solderability of Tinned Surfaces*

A surface which has been coated with tin or solder by dipping it after suitable cleaning and fluxing treatments is ideal for soldering since all that is necessary is to bring molten solder into contact with it and allow its

coating to merge in the solder. There are, however, other methods of coating metals with tin or solder which may be preferred for their convenience in particular circumstances although their solderability may not be as good as that of hot dipped coatings. Among such alternative coatings may be mentioned:

- (i) electrodeposition
- (ii) chemical replacement
- (iii) stannising
- (iv) spraying

(i) *Electrodeposited Coatings of Tin and Solder*

Electrodeposited coatings may be of any desired thickness: The baths in common use are the alkaline stannate and the acid stannous sulphate but a number of other baths are also available. Very thin coatings, like replacement coatings, are not effective for soldering. For good solderability after long storage the following thicknesses have been recommended ²¹:

on steel	0.0002 inches (0.0050 mm),
on copper	0.0003 inches (0.0075 mm),
on brass.	0.0005 inches (0.010 mm).

It has recently been claimed ²⁹ that coatings of tin-lead alloy (30 per cent tin) deposited from a fluoborate bath to a thickness of only 0.0002 inches (0.0050 mm) retain their solderability even after several months of storage; it is possible that there is less diffusion of the basis metal through the lead alloy coating than through the pure tin and that as a result, the alloy coating remains less contaminated and therefore less liable to oxidation.

(ii) *Chemical Replacement Tinning*

Chemical replacement tinning is usually applied to small articles such as pins, eyelets, tags and wire hooks. A quantity of the articles is placed in a suitable vessel and boiled for some minutes or even an hour or two with a salt of tin. The coatings can be produced upon steel, brass and copper surfaces and the thickness is usually of the order of ten to twenty millionths of an inch (0.00025 mm). When newly applied, replacement tinned coatings may solder with about the same facility as freshly cleaned bare metal but their solderability rapidly declines, probably by diffusion of the base metal upwards through the coating. Heating for 30 minutes at 150° C assists the diffusion and on brass or copper the underlying surface may become visible; a repetition of the replacement treatment restores the bright tin appearance.

(iii) "*Stannising*" and *Alloyed Coatings*

Stannising or the coating of steel, copper and brass with tin deposited from the vapour of stannous chloride at 500°C in an atmosphere of hydrogen, gives coatings which are completely alloyed with the basis metal and are readily soldered¹⁴. Similar fully alloyed coatings can be obtained by a replacement process in which the tin is deposited from a molten mixture of chlorides and bromides of tin mixed with alkalis, zinc and perhaps other metals. The solderability is inferior to coatings containing free tin.

(iv) *Sprayed Tin Coatings*

Sprayed coatings are applied to surfaces below the melting point of the tin or the alloy which is being sprayed. There is therefore no alloying between the tin or solder and the base although some diffusion probably occurs. There is no predisposition to soldering but the presence of the sprayed coating, which is generally thick, of the order of 0.001 or more inches, means that there is amply sufficient solder or tin on the surface to effect the soldering.

§ 5. TREATMENT OF OXIDIZED SURFACES

(a) *Aluminium*

The normal pretreatment and fluxing do not suffice to remove the oxide film and to leave a bare metal surface because the aluminium reacts vigorously with air, water or other oxygen-containing substances. The recommended method of soldering this metal is to cover it with molten solder and then scratch away the oxide film so that the solder comes into contact with the bare metal before oxidation can occur. The solder should contain about 70 per cent of tin and 30 per cent of zinc. The temperature should be in the region of 400°C and in order to minimise oxidation it is an advantage to have a cover of fused salts, generally the chlorides and fluorides of the alkalis.

Another recommendation is that the oxide film should be artificially thickened by treatment with a mixture of phosphoric and nitric acids for one minute; the acid is then washed off and the dried surface is said to be solderable.

Ultrasonic vibration applied to a heated soldering bit containing abrasive material is effective in removing the oxide film and appliances for this

purpose are now available commercially. The bit is applied under molten solder of the 70/30 tin-zinc type. Surfaces "tinned" by this method are frequently difficult to solder without further application of the ultrasonic type of soldering bit.

(b) *Copper Alloys Containing Beryllium, Aluminium, Silicon*

The alloying additions mentioned are all readily oxidised and even when present to only a few percent have a most deleterious effect on solderability. The treatment recommended for aluminium is sometimes capable of bringing about wetting but the adhesion is usually rather low.

(c) *Glass and Ceramics*

While glass, porcelain and other vitreous and ceramic surfaces are not wetted by tin or ordinary tin-lead solders they can be specially prepared so that a solderable deposit will adhere to them. The usual method is to flash a thin deposit of silver on to the specially cleaned surface by BRASHEAR's method or by painting on a suspension of silver oxide in oil of lavender or a similar heavy oil which when strongly heated will reduce the silver and leave it firmly adhering to the ceramic or glaze. The first thin film of silver is then thickened by electrodeposition of silver or copper to a thickness sufficient to allow of soldering in the usual way.

It has recently been claimed that an alloy of tin with its own weight of indium can be made to adhere to very clean glass. The alloy is applied at about 140° C and allowed to cool extremely slowly. During solidification, which occupies the range from 127° C down to 117° C, the alloy becomes pasty and adhesion to the glass develops.

§ 6. WETTING OF METALS BY TIN AND SOLDER

For simplification we will consider first only one surface, that is, one half, of a soldered joint consisting of steel, iron-tin compound and solder. Unprepared steel dipped in molten solder may be left there for a long time but solder does not adhere to it. Clean steel, coated with flux and then dipped, rapidly acquires a thin coating of solder. In some cases the coating of solder may appear "greasy" or rippled because the molten solder, as it drains under gravity, may form irregularly into streaks, like water on a greasy surface.

In the first mentioned case, when the steel fails to acquire a coating of solder, it is observable that the surface of the molten solder is not, during the dipping operation, normal to the steel but is curved sharply downwards

and, below the level of the solder surface, lies tangentially against the steel. Where the steel acquires a coating of solder the surface of the molten metal curves upwards in a meniscus that is located at an appreciable distance above the level of the solder surface. From the similarity of behaviour to that of water in contact with greasy glass or with clean glass, the word "wetting" is used to describe the behaviour of the molten solder ⁶. Where the coating appears "greasy", there may have been only partial wetting or it is possible that wetting may have been followed by partial "de-wetting".

(a) "*Pores*" in Tin Coatings

Oxide, carbon, graphite, siliceous or other non-metallic particles are not wetted by tin and when these substances are present in iron or steel surfaces, the coating of tin may show small discontinuities or pores at their sites. Provided that the non-wetting particles are small they may be bridged over by the tin, both while it is molten and when it has solidified. CHALMERS ⁵ found that for pores to be stable in tin coatings, they must have a minimum diameter of 0.7 of the thickness of the coating. These non-metallic inclusions are not the only causes of pores; gas bubbles at the metal surface may prevent contact with the tin; such bubbles may form there by expulsion of hydrogen, which is absorbed plentifully during pickling and fluxing, or may have their origin in the vapourisation of moisture from the flux or in gaseous products of the fluxing action and be mechanically entrained in the molten tin.

JONES ¹⁸ found that molten tin would not wet copper at surface inclusions of cuprous oxide but reduction of these inclusions to metallic copper by means of hydrogen enabled tin to adhere to them. He also established that this initially nearly perfect wetting did not survive prolonged or repeated immersion in molten tin; the surface showed strong de-wetting due to the tin dissolving the superficial film of reduced copper and exposing the underlying oxide that had not been reached and reduced by the hydrogen.

(b) *Formation of Compound during Spreading*

On a plate of steel, copper or other solderable metal, there is, during wetting by solder, the simultaneous formation of compound with the tin in the solder ¹⁰; some of the tin becomes fixed to the solid metal in a solid crystalline formation. The tension in the molten solder surface does not prevent tin from passing into the solid metal; as the process continues, the crystalline compound layer grows thicker and more irregular; the boundary of the

molten metal over this area ceases to exist as a continuous envelope and it is replaced by a zone of solid compounds, attenuating upwards into the solder and downwards into the solid metal; some compound is formed in the solder and when the saturation point is passed it may appear in crystalline form, coming out of the liquid metal. The surface of the molten solder drop is no longer a continuous envelope in tension as it would be on a glass surface; the envelope now exists only from meniscus to meniscus over the free surface of the molten drop of solder. The solder spreads outwards continually under hydrostatic pressure and when this force has ceased to be important any longer because of flattening of the drop, spreading continues by diffusion both downwards into the metal and outwards.

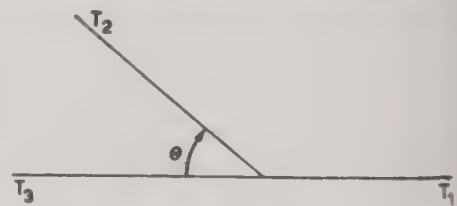
(c) *Effect of Surface Roughness on Spreading*

CHALMERS and WADIE⁶ pointed out that the simple theory of surface tension was inadequate for the wetting of metals by tin because the solid surface was not ideally smooth. On a smooth solid surface the equilibrium at a liquid boundary is the balance of the tension between the liquid and the solid and the opposing combined tensions in the liquid/air surface and the liquid/solid interface.

In the Fig.

$$T_1 = T_3 + T_2 \cos \theta \quad (i)$$

But when the rough surface is n times greater than the projected area of the solid surface



$$nT_1 = nT_3 + T_2 \cos \theta \quad (ii)$$

Let θ be the angle of contact for a smooth surface and θ_1 that for a rough surface ($n > 1$)

Then

$$T_1 = T_3 + T_2 \cos \theta$$

and

$$nT_1 = nT_3 + T_2 \cos \theta_1$$

or

$$n(T_1 - T_3) = T_2 \cos \theta_1$$

and

$$T_2 \cos \theta = \frac{T_2 \cos \theta_1}{n}$$

$$\cos \theta_1 = n \cos \theta$$

When $\theta < 90^\circ$, corresponding with a tendency to wetting, increase of n may increase $\cos \theta$ to a value greater than 1, that is, wetting may be

complete. When $\theta > 90^\circ$, increase of n increases the negative value of $\cos \theta$ and so increases θ , that is, causes less wetting. That is, roughness increases whatever tendency would exist on a smooth surface: a wettable surface wets more easily, and poorly wettable metal is more difficult to wet. Similarly if n is less than unity, θ_1 is greater than θ , that is, wetting is less complete: this covers the case of a surface with non-tinnable inclusions in it.

(d) *Surface Capillarity and Spreading*

Evidence that surface roughness or capillarity can promote spreading and wetting was obtained by PARKER and SMOLUCHOWSKI²⁶ for molten silver on steel. They machined three sets of parallel grooves on a sheet of special steel containing 6 per cent of molybdenum in order to prevent the transformation from the α to the γ form at the high temperature of their tests. In the first set of grooves the sides converged at an angle of 120° , in the second, the angle was 90° , and, in the third, it was 60° ; all three sets of grooves were of the same depth, namely, 0.005 inches.

The sheet was dipped vertically into molten silver and it was observed that there was no appreciable rise of silver in the grooves of 120° ; in the 90° there was a rise of about one inch above the level of the molten silver, and in the 60° grooves there was a rise of two inches.

In another test, sheets of the steel were prepared with a variety of finishes, formed into boats and placed in a combustion tube. In the middle of each boat a drop of silver was placed and its spreading behaviour was observed. With a coarse emery finish there was very little spreading and not very much upon a sand-papered surface; on polished surfaces the spreading was slight, but on nitric acid etched surfaces the silver spread unchecked over the entire surface of the boats, including the internal vertical sides, the outsides, and across the underside. The silver spread more rapidly along the grain boundaries of the steel than over the surface of the grains of iron.

(e) *Electrochemical Action Precedes Spreading*

LATIN studied the influence of fluxes on the spreading power of tin solders on copper¹⁹. With zinc ammonium chloride flux, he observed that around the drop of molten tin or solder there was a grey halo extending further outwards into blue. A similar effect was seen on the surface of copper when heated in contact with zinc chloride which had previously been strongly heated with tin or solder. LATIN immersed a copper strip in fused stannous chloride floating on molten tin and made electrical connection outside the

bath between the copper and the tin. The surface of the copper instantly changed to grey and then became silvery in colour, due to a deposit of tin. The copper became the positive pole and it was inferred that the chloride ions were liberated at the molten tin anode and so maintained the supply of stannous chloride. The first deposition of tin on copper during soldering, therefore, appears to be the result of a chemical replacement action in fused chlorides or other electrolyte. Replacement tinning of copper and of steel by immersion in fused salt mixtures of stannous chlorides with sodium and other chlorides have been known for several years, and have been employed commercially for the production of thin tin coatings on threaded parts with a view to avoiding the clogging of the threads of fine grooves with molten tin which is difficult to avoid when tinning by dipping in the usual way. The "Stannising" process¹⁴ produces thin deposits of tin on copper and steel parts by exposing them to an atmosphere of stannous chloride vapour mixed with hydrogen at about 500° C.

(f) *Spreading and Alloying*

LATIN found that pure lead spread rapidly on copper at 350° C under resin or preferably halide fluxes; a drop of lead spread to the edge of the specimen. The surface tension of lead in hydrogen at 350° C is 441 dynes per cm compared with 550 dynes per cm for tin at 250° C. He took this to indicate that the work of adhesion, lead to copper, must be high although there is no alloying action to aid the wetting, but he remarked that the decrease in contact angle with rise in temperature in the case of both tin and solder on copper "is possibly due to increased readiness of alloying."

(g) *Area of Spread Tests for Solderability*

The area that becomes covered with solder when a fixed quantity of it is heated to a particular temperature while lying upon a flat plate of the metal in question, has been used as a means of assessing the soldering characteristics of various alloys.

In one version of the test, the solder in the form of a standard pellet is placed at the centre of the metal specimen which is one inch square and mounted upon three needle points on a spring-mounted stage which can be raised by a cam movement so that the pellet of solder is brought up to and makes firm contact with a soldering bit (Fig. 149). The soldering bit carries a nichrome tip of the same size as the pellet of solder and into this tip a thermocouple is fitted indicating its tempe-

perature. Within a few seconds the solder melts and spreads out in all directions. The spreading may be allowed to continue to the maximum or for a prescribed length of time only. The area of spread is then computed with a planimeter.

Variations may be made in the type or quality of the solder, the flux, the basis metal, and in the temperature of the bit. The test gives useful indications of the merits of the various factors but is not as sensitive as could be wished (Fig. 150).

(h) *Surface Tension of Solders*

The surface tension of tin was found by BIRCUMSHAW² to be 550 dynes/cm at 250° C in hydrogen; this is equivalent to a work of cohesion of 1100 ergs/sq. cm so that for complete spreading, the work of adhesion between the tin and the solid metal would have to exceed this figure. For a solder of eutectic composition the surface tension in hydrogen is 490 dynes/cm equivalent to a work of cohesion of 980 ergs/sq. cm, that is, 120 ergs/sq. cm less than tin. LATIN concluded¹⁹

that the smaller work of cohesion in eutectic solder as compared with tin, is the cause of the better spreading of eutectic solder; he also inferred that since the work of cohesion in 50/50 tin-lead solder is lower than in eutectic solder, spreading should be better in this case also, but this was not found to be the case in EARLE's tests with the Kollagraph.

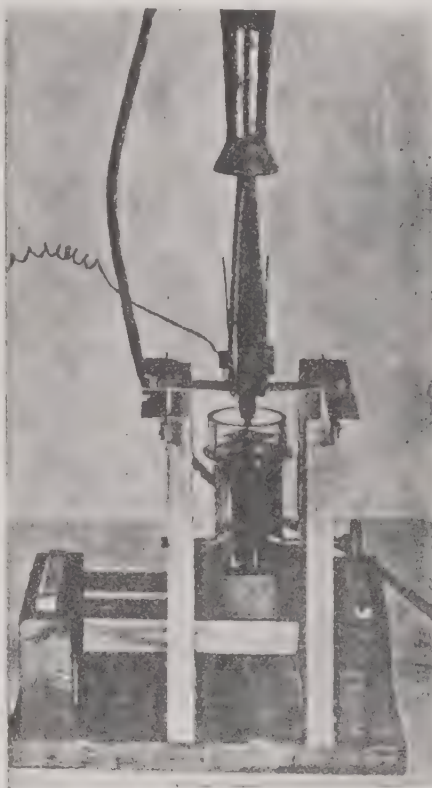


Fig. 149. Apparatus for determining the spreading qualities of solders.

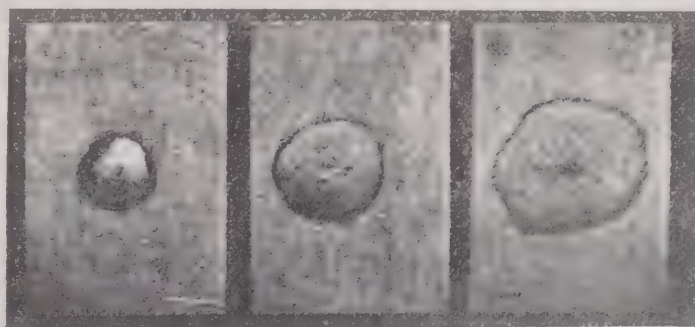


Fig. 150. The results of some typical spreading tests.

(j) *Measurement of Wetting by Solder*

In practical soldering it is desirable that the solder should spread over and wet the metal without any appreciable lapse of time. EARLE considered ¹¹ that when wetting by solder occurred within one-fifth of a second, it could for practical purposes, be regarded as instantaneous and he adopted this

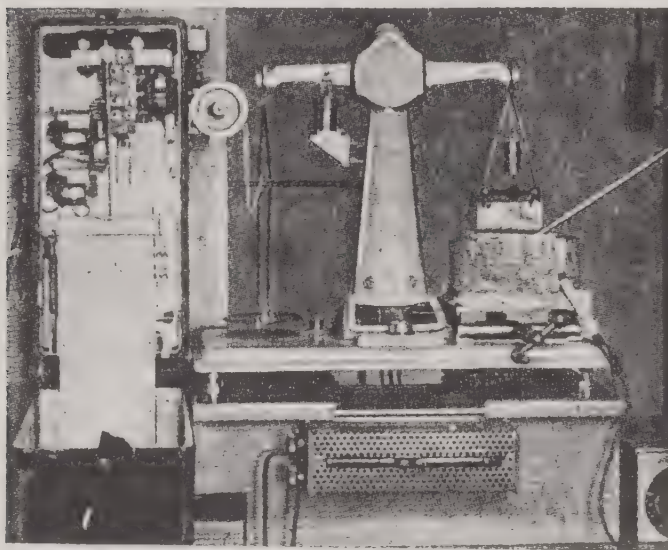


Fig. 151. The Kollagraph measures and records the jointing capacity of soldering systems.

as a criterion for the comparison of soldering properties. He determined the lowest temperature at which various solders and fluxes would instantaneously wet a number of different metals under standardised conditions; this he described as the „minimum effective wetting temperature” (M.E.W.T.). The apparatus was termed the Kollagraph and is shown in Fig. 151. A flat plate of the metal

under test is suspended, with its lower edge horizontal, above a pot of molten solder and forms the load on one arm of an automatic balance. When the load is increased, the position of balance is rapidly restored by the paying out of a fine chain. During a test, the bath of molten solder is raised until the solder surface makes contact with the metal plate. The first effect in many cases is that the metal plate floats and as a result the load on the balance decreases momentarily, but, after a fifth of a second, or perhaps a little longer, the solder wets the plate and begins to exert a downward pull on each side. This pull is rapidly counterbalanced by the release of chain and at the same time a pen moving in sympathy with the chain drum records the movements upon a continuous chart, running at a quarter of an inch per second.

(k) *The Kollagraph*

The records obtained, called Kollagrams, are of the type shown in the Fig. 152. The Kollagram on the right shows an upward thrust persisting

for nearly 4 seconds before the pull is developed; the pull increased for the next $5\frac{4}{5}$ th seconds and reached equilibrium at 258 dynes/cm. In this instance the solder contained 40 per cent. of tin, 60 per cent. of lead, the temperature was 240°C , and the flux on the plate of copper was zinc ammonium chloride. The Kollagram on the left was made with the same materials but the temperature was 350°C ; the wetting was instantaneous

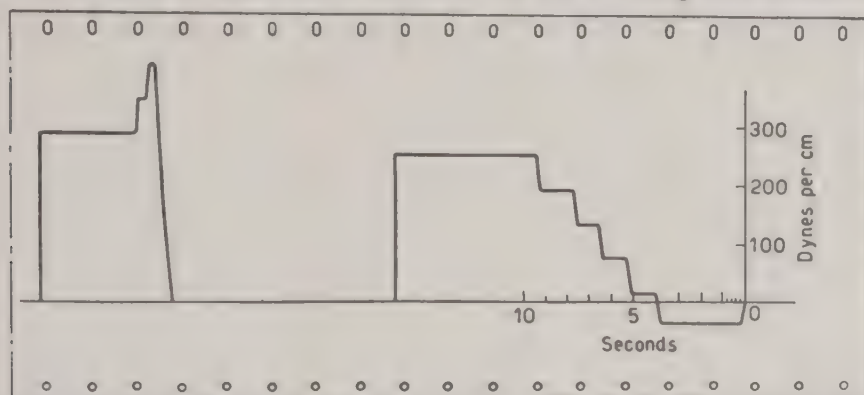


Fig. 152. Typical Kollagrams showing quick wetting at 350°C (left) and delayed wetting at 240°C (right).

but, in this case, the inertia and delayed response of the apparatus caused the balancing load to overshoot before equilibrium was attained. The pull ultimately developed is the interfacial tension of the solder for the metal under the particular conditions of each test. Using the strongly active zinc ammonium chloride flux, the maximum pull was always developed practically instantaneously, but with resin an appreciable time was sometimes needed.

It was confirmed that the mean meniscus rise on the two sides of the plate was proportional to the surface tension developed. For tin-lead solders in the range 63 to 18 per cent. tin, the meniscus rise averaged about 3.1 mm on copper with zinc ammonium chloride flux; this corresponds with a mean interfacial tension of 300 dynes per cm and this value did not vary significantly over that range of tin content. On the other hand, for an alloy with 5 per cent. tin, 4 per cent. antimony and 91 per cent. lead, the meniscus rise was 1.1. mm and the maximum tension was 120 dynes/cm.

EARLE obtained smooth variation of M.E.W.T. with thickness of the basis metal and with tin content. Fig. 153 shows the value for brass from 0.003 to 0.024 inches thick and for tin-lead solders ranging from 20 per cent. tin up to eutectic, 63 per cent. In the upper diagram the broken line is the liquidus of the solders; it is seen that with eutectic solder on brass of 0.003 inch thickness, the M.E.W.T. is 18°C , above the solidus/liquidus

temperature. For copper of this thickness the M.E.W.T. appears to be a degree or two below the liquidus in the range approximately 50 to 40 per cent. of tin, but with 30 per cent. of tin the M.E.W.T. exceeded the liquidus

by 6° C, and by 27° C for 20 per cent. tin content.

For thicker specimens it was the rule that M.E.W.T. values were higher unless the specimen was pre-heated. Thus, a sheet of 0.012 inch thickness at 120° C required solder at the same temperature as sufficed to wet a *cold* specimen of 0.004 inch in the allotted time.

Fig. 154 shows that the eutectic solder has the lowest M.E.W.T. with copper strip. This was also true for other metals including tinplate. Pure tin (m.pt. 232° C) was not better than 30 : 70 tin-lead solder which has a slightly higher

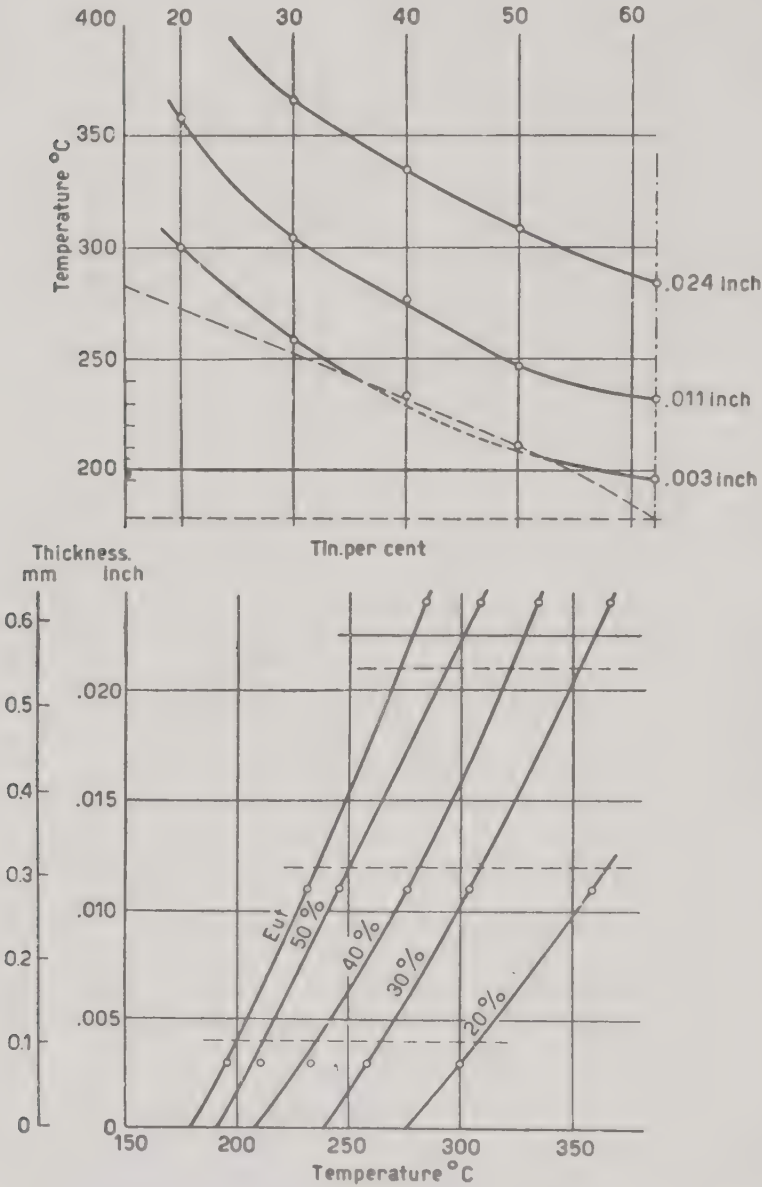


Fig. 153. Brass vs. tin-silver-lead "T" solder, Z.A.C.flux. liquidus (250° C).

(1) *Kollagraph and Solderability of Metals*

Kollagraph tests were made on tinplate, blackplate (plain steel), terneplate

(tin-lead coated steel), copper, brass and zinc. Tinplate was wetted at lower temperatures than the other metals by all solders. The tin-lead solder (free from antimony and other additions) wetted all the metals readily. Addition of antimony, up to 6 per cent. of tin content, was decidedly deleterious to wetting on copper,

but did not affect tinplate and terneplate; as these metals are steel which has already been wetted with tin or solder, it is scarcely necessary to apply the test to them but it may be useful as a practical indication of the readiness with which their coatings merge with the particular solder applied to them. Brass was wetted more easily than copper whether antimony was present or not. Zinc could not be dependably soldered with antimonial solders. Addition of just under 1 per cent. of silver to 40 per cent. tin solder appeared to be an improvement when soldering copper with a resin flux for it gave a

M.E.W.T. value equal to that of the tin-lead eutectic.

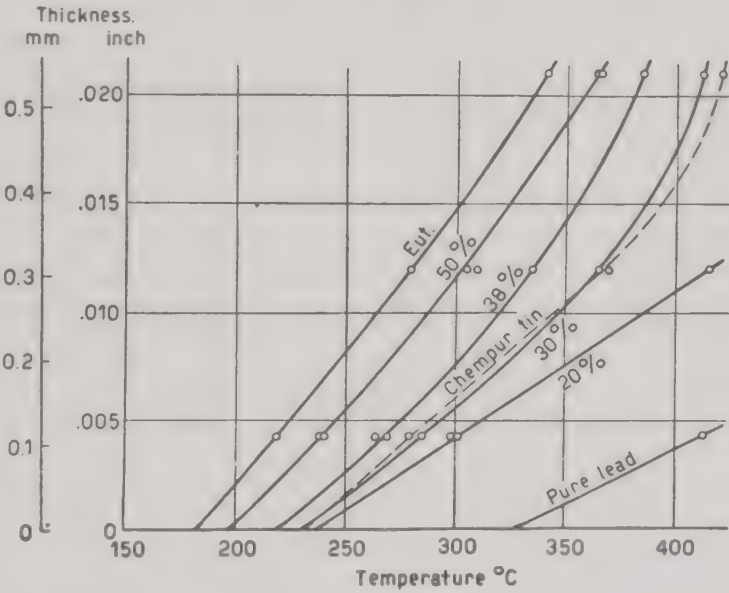
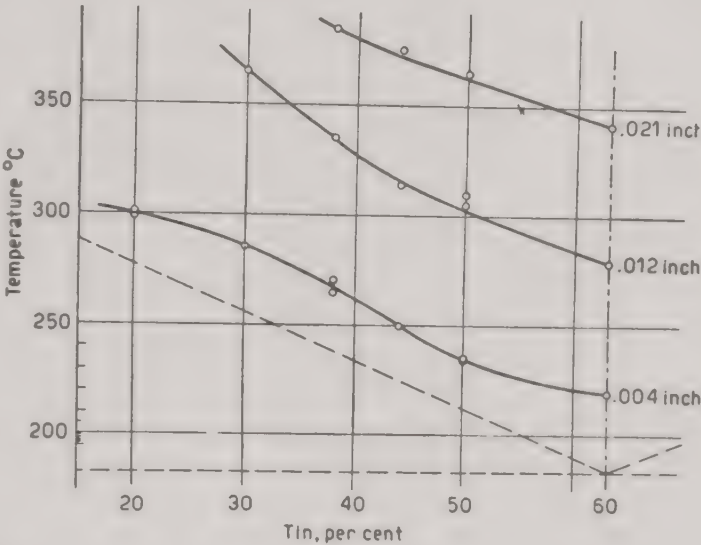


Fig. 154. Copper vs. high-purity tin-lead solder, Z.A.C.flux.

(m) *Capillary Rise Test for Solderability*

SCHUMACHER, BOUTON and PHIPPS devised a method for distinguishing between the activity of solders at chosen temperatures upon various metals



Fig. 155. SCHUMACHER's apparatus for testing solders

and in the presence of any selected flux²⁸. Two wires of the metal are twisted together round each other so that the length of a whole twist is one inch (Fig. 155). The pair of wires is then held vertically in pliers, dipped into a pot of flux and then lowered on to the surface of molten solder of the required composition and at the selected temperature. As soon as the wires touch the surface the solder climbs in the capillary space between them to a definite level which is characteristic for the peculiar circumstances of each test. It is possible by this means to make comparison of each variable in turn, and to examine the influence of temperature or of flux upon the height of climb of any particular solder upon a metal or upon a pair of

wires of different metals, such as brass and steel. As a result of a large number of tests, it was established that tin-lead solders of the eutectic composition (63 per cent. tin and 37 per cent. lead) climbed higher than any other composition. It was also found that, whatever the proportions of the tin and the lead in the original solder, the solder at the top of the wires after a test was always a very close approximation to the eutectic composition provided that the proportion of the tin to the lead in the original solder exceeded 30 per cent.

(n) *Flow Dependent on Temperature Gradient*

This fact suggests that there is some sort of fractionation of the constituents in the solder under these conditions resulting in the more leady constituents being segregated to the bottom. This is no doubt due to the fact that when conditions have settled down, near the end of each test, there is a temperature gradient from the foot of the pair of wires to the top; because no constituent in the solder can flow where the wires are not at least as hot

as its own particular melting point, the highest melting constituents, those richest in lead, separate near the base of the wires, while the lowest melting (eutectic) portion is able to climb higher than any other.

This state of affairs is of common occurrence in ordinary soldering operations using the copper soldering bit. There is intense heating of the metal under the bit and close to it on each side, but the temperature falls rapidly by conduction into the adjoining mass of metal; the eutectic constituent should therefore penetrate furthest into the joints.

(o) *Fractionating Effect in Soldering*

In general then, where a big temperature gradient exists while the soldering is being done, there is a gradation of composition in the direction of that gradient. An example is the automobile radiator where the soldering is done by dipping each face of the block of strips or thin walled tubes into a bath of molten solder. Solder enters the capillary spaces between the tubes or strips of copper or brass and climbs into a space which is chilled by conduction to the interior of the block. The leady constituents will tend to stop near the bottom, that is at the face of the block, and the innermost solder which has penetrated furthest will be richest in eutectic composition. This segregation of the eutectic into the block may cause some impoverishment of the solder in the bath in respect to tin content.

Another factor tending to cause impoverishment is the removal of tin during the formation of the intermetallic compound in the joints. Which effect is most serious must depend on the particular circumstances in each case; in practice it means that the tin content of the solder in the joint may often be two or three per cent higher than that of the solder in the bath, and if the percentage of tin in the joints is not to decline progressively below the desired figure, the solder with which the bath is replenished should be correspondingly richer in tin.

(p) *Penetrative Powers of Solders*

LATIN investigated²⁰ the penetrating power of solders of various tin contents between flat metal plates, but comparison of their penetrating powers was obscured to some extent by the necessity of varying the temperature of application to compensate for the different liquidus temperatures of the different compositions. While 250° C allows a solder of the eutectic composition to spread rapidly, it is much too low for a solder containing, say, 70 per cent. of lead and having a liquidus at about 270° C. Latin measured the penetration power of each solder at 60° C above its liquidus, that is to say, at 243° C in the case of the eutectic and at 330° C

for the 70 per cent. lead solder. It was not possible therefore to deduce from this work a relationship between the tin content and the penetration power of solders. While the SCHUMACHER, BOUTON and PHIPPS' test shows that the eutectic constituent in solders climbs higher than other proportions of tin and lead, this appears to be a consequence of the temperature gradient existing in the wires; whether the surface tension of the eutectic is higher than that of other solders of tin and lead is not established by such a test. EARLE's Kollagraph failed to show any important differences in surface tension of solders ranging in tin content from 63 per cent. down to 18.5 per cent., but it seems likely that was due to the steep temperature gradient which existed in the plates under test. Under practical conditions there is generally a fairly steep temperature gradient and the depth of penetration of the solder into the joint will mainly be governed by the extent to which eutectic is available for the filling of the joint.

§ 7. THE STRUCTURE OF THE BOND IN SOLDERED JOINTS

(a) *Compound Formation*

It has already been mentioned that there forms between the solder and the metal which is soldered a layer compounded of tin from the solder and the metal of the solid surface. Although there is lead in solders this metal does not form compounds with iron, copper and zinc, for example, and it merely serves to dilute the tin which is present so that, at any rate on copper, less of the compound is formed than if the tin were there alone. The entire surface of the metal becomes covered with the compound but the thickness is less when lead is present, presumably because the tin has to diffuse through a leady mass in order to reach the surface of the metal. The compound layer is the link eventually between the solder and the solid surface; the strength of the bond, or the adhesion, is dependent upon the physical characteristics of the compound, such as its thickness, its crystal size, structure and orientation, and its tensile strength.

(b) *Adhesion without Compound*

These factors will be considered, but first it must be stated that CHADWICK has shown ⁴ that excellent adhesion can be obtained between lead and copper although lead forms no compound with copper: the adhesion is comparable in amount to the strength of the lead itself. In order to obtain wetting and adhesion between copper and lead, it is necessary to clean the copper thoroughly and carry out the melting of the lead and subsequent heating in an atmosphere of hydrogen and preferably at temperatures upwards

of 500° C; when resin or a halide flux is used, LATIN found that spreading occurred at 350° C or higher.

§ 8. NATURE OF COMPOUND LAYERS

The compounds which form between tin and other metals have been the subject of much study and, generally, are known for equilibrium conditions but not necessarily for the very much shorter times which suffice for the making of soldered joints.

(a) *Tin-Iron Compounds*

The equilibrium diagram of the compounds which form between tin and iron has been worked out by PREECE and EDWARDS, and JONES and HOARE ⁶ have elaborated further details. From this work it appears that with fairly high tinning temperatures, such as are met with in the manufacture of tinplate by dipping steel sheets into molten tin for a second or two, there is formed a layer of the compound FeSn_2 , the thickness of which is generally of the order of about 0.00001 inches (0.00025 mm) and once this layer has formed the growth in thickness is slow; the first formed compound acts as a barrier to the diffusion of the two metals. Increasing the time of contact at the tinning temperature by several times makes very little difference to the thickness. One contributing factor in this is that the tin-iron layer is only very slightly soluble in the tin so it is not washed away or removed from the iron surface. The tin-iron layer is extremely hard and brittle and would possibly form a very weak and unsatisfactory bond between the very ductile tin or solder and the harder, but still ductile, steel or iron. It is fairly certain, however, that there are extremely thin transition layers between the compound and metals on each side of it; on the iron side there is some FeSn and on the tin side there is a layer of tin which is saturated with FeSn_2 . The strength of the bond between each adjacent pair of phases would, therefore, affect the joint strength but although direct measurement of these bond strengths has not been made, the evidence of the fracture surfaces shows that the weakest of them all is the compound FeSn_2 , since joints break in this layer and not on either side of it ⁴.

(b) *Tin-Copper Compounds*

The bond between copper and tin or solder is similarly through a layer of compound, which DANIELS identified ⁹ as mainly Cu_6Sn_5 , with a much thinner layer of Cu_3Sn between it and the copper (Fig. 156). CHADWICK found ⁴ that prolonged heating at 500° C gave rise to yet another layer

between these and the copper, namely, Cu_4Sn (or $\text{Cu}_{31}\text{Sn}_8$), and there is no reason to suppose that the full range of compounds which can form under equilibrium conditions between the two metals at this temperature is not represented. Again the question arises as to the relative strengths of the bonds between these adjacent pairs of phases, but there is no direct information about them; joints between the solder and copper appear to break

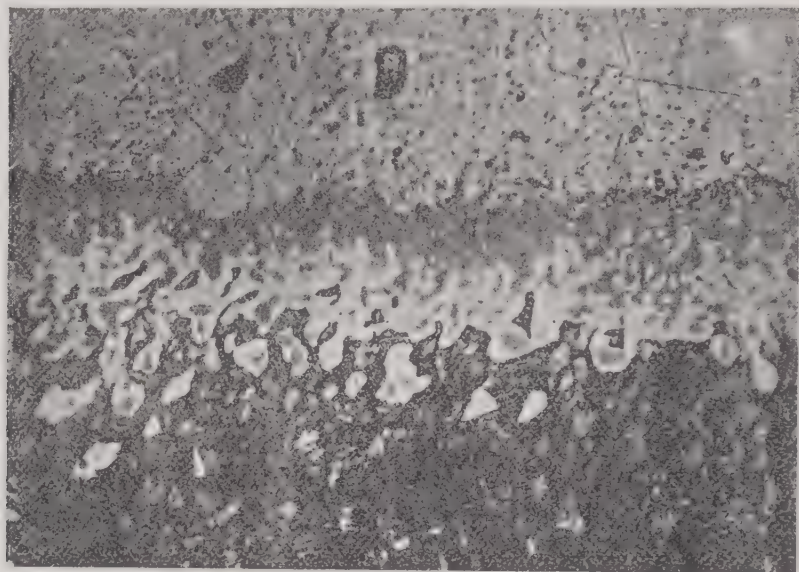


Fig. 156. Alloy layer between tin and copper after tinning for 30 seconds at 450°C . Tin (dark ground) above Cu_6Sn_5 , then Cu_3Sn , and copper beneath ($\times 1000$).

in the Cu_6Sn_5 layer, but this is always far thicker than any of the others and it would be difficult to detect traces of the extremely thin layers of other compounds.

(c) *Solubility of Tin-Copper Compound in Tin*

DANIELS emphasised that the compound layer formed in tinning copper breaks up continually and dissolves slowly in the molten tin. When the temperature of tinning is low and the duration of it is short, almost all the compound formed is concentrated close to the copper and there is a coating of substantially pure tin above this. With higher temperatures and longer times of contact at tinning temperatures, there is present tin-copper eutectic having the melting point of 227°C and containing 0.7 per cent. of copper; later on crystals of Cu_6Sn_5 separate from the liquid phase. DANIELS thought the presence of these crystals in the molten tin and at the surface of the copper might prevent any tendency to de-wetting and could therefore

reduce de-wetting of the coating but the practical difficulty arises that they may cause the coating to be gritty in appearance.

On brass the compound layer forms rapidly due to the ease with which the zinc constituent dissolves in molten tin and the correspondingly more rapid attack of the copper at the same time. In one respect this action is beneficial²⁴, since it increases the creep strength²² in the solder but the joints may fail through their brittleness during cooling down to room temperature.

(d) *Compound Growth in Joints*

SWANGER and MAUPIN examined³¹ the changes which occur in soldered joints during long storage at elevated temperatures. The joints were made between copper tubes soldered into copper sleeves as in ordinary domestic hot water systems and they were maintained at 250° C for periods up to one year. With 50/50 tin-lead solder there was a continued growth of



Fig. 157. Photomicrographs showing the growth of intermetallic compound in a soldered copper joint maintained at 250° F (121° C) for one year (SWANGER and MAUPIN).

(a) Original structure of joint.

(b) Structure of the same joint after 7,500 hours at 250° F (121° C).

tin-copper compound, both Cu_6Sn_5 and Cu_3Sn being formed. These crystals were sufficiently large for tests of their KNOOP hardness to be made on them and values of 200 were obtained, as compared with 22 for the original solder without any compound in it. The joints as would be expected,

therefore, were very brittle and ruptured under tension, whereas freshly made joints with very little compound in them stretched under load without breaking. The formation of the tin-copper compound, continuing for so long, reduced the tin content of the layer of solder between the copper surfaces and as can be seen from the photomicrographs the proportion of lead was much higher than in the beginning of the tests (Fig. 157).

§ 9. ADHESION OF ANTI-FRICTION ALLOYS TO TINNED SURFACES

A type of bond that resembles a soldered joint is that between a tinned metal shell and a lining of anti-friction alloy. The chief point of difference is that the anti-friction alloy is applied in the liquid state instead of as a solid. The shell, usually of steel or bronze, is first tinned, preferably with pure tin but sometimes with a tin-lead solder, and then the molten alloy is cast in position on to the heated shell and allowed to solidify²⁷. The anti-friction alloy may be based mainly on tin, with about ten percent of antimony and copper, or it may contain any proportion of lead up to about 75 per cent., with rather higher antimony than in the tin-base alloys; all the alloys, however, are miscible with the tin of the tin coating on the shell. Pouring of the alloy is carried out at a temperature of around 430° C, or higher in the case of the lead-base alloys. The duration of the cooling is, therefore, considerably longer than in soldered joints and as the rate of formation of compound is also increased at higher temperatures there is generally more compound formed than in soldering.

(a) *Segregation of Tin-Copper Compound at the Bond*

The presence of copper to the extent of two or three per cent in the anti-friction alloy, that is to say, well above its saturation limit in the tin constituent, is productive of crystals of Cu_6Sn_5 which may segregate at or close to the bond for two reasons^{12, 13}. Firstly, because it is usual to arrange matters so that cooling begins from the outside of the shell and thereby ensure that the solidification begins on the shell and proceeds into the anti-friction metal. This ensures that shrinkage voids will occur not at the bond, where they would reduce the area of adhesion, but will be situated on the inner side of the lining where metal is going to be removed during the final machining. The tin-copper compound being of high melting point, about 415° C, crystallises first and is largely precipitated on the shell, therefore (Fig. 158). Secondly, in some cases the casting is carried out

centrifugally in order to obtain a more dense product, and because the Cu_6Sn_5 is a heavy constituent it is concentrated towards and at the bond.

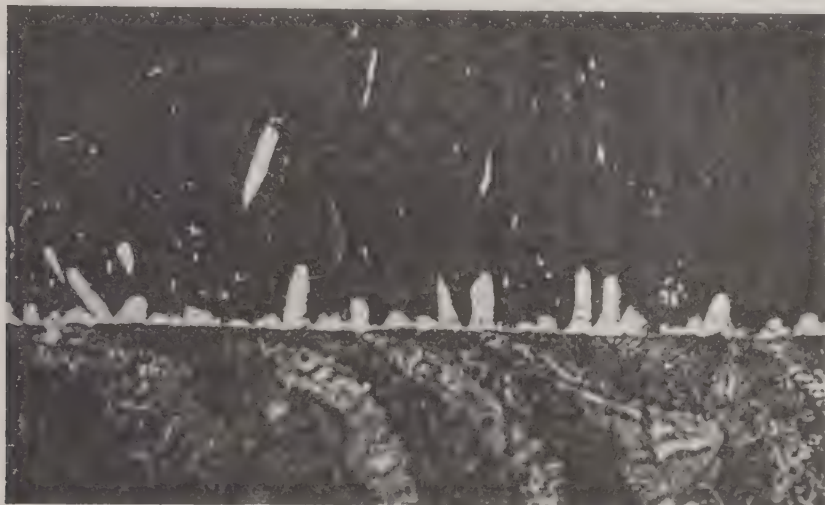


Fig.158. Whitemetal above bronze showing layer of Cu_6Sn_5 deposited on the bond ($\times 500$) (FORRESTER and GREENFIELD).

(b) *Failure in the Bond*

FORRESTER and GREENFIELD found that the compound at the bond of an anti-friction alloy cast upon a tinned steel base was FeSn_2 and was usually

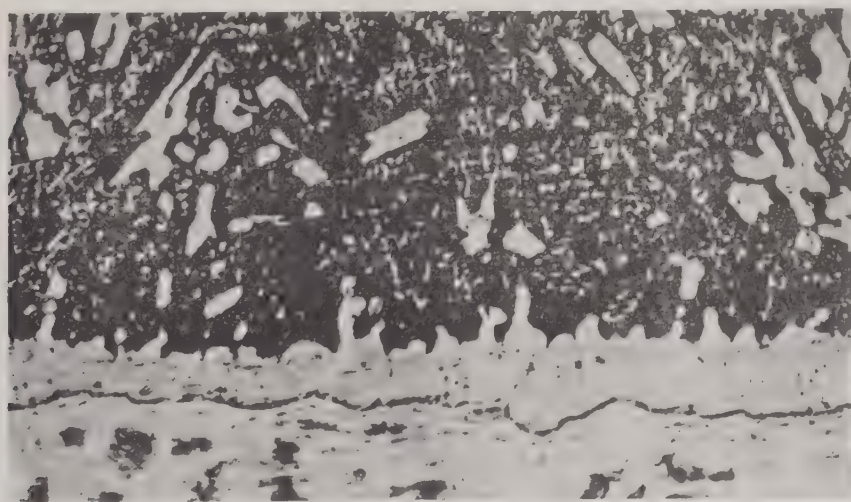


Fig. 159. Chain of Cu_6Sn_5 crystals deposited from whitemetal containing 7% Cu. The crystals are located upon an abnormally thick layer of FeSn_2 produced by tinning for 1 hour at 450°C ($\times 400$).

so thin that it had little or no effect upon the adhesion. On the other hand, holding at casting temperature or lower for some hours caused the FeSn_2 layer to grow in thickness (Fig. 159) and the crystals themselves to grow coarser, and the effect was to decrease the bond strength. On a bronze base the compound was mainly Cu_6Sn_5 , present as large needles which caused marked brittleness. In a series of tests of adhesion of white anti-friction metals to steel or bronze shells, FORRESTER and GREENFIELD found failure in the compound layer in the bond but never in the anti-friction alloy itself.

(c) *Factors Affecting Bond Strength*

(i) *Temperature*

PRYTHERCH ²⁷ studied bond strengths for a number of anti-friction alloys, bonded to steel and copper, over a range of test temperatures up to 150° C. He noted the tendency for a strong bond at the end of steel test-pieces to result in a failure in the anti-friction metal rather than in the bond, and he

avoided this by bonding the rods to the ends of cylinders of anti-friction metal of greater diameter than the rods themselves (Fig. 160); when such assemblies did fail in the alloy they pulled out a cone of the alloy. At room temperature with test pieces of this shape, he obtained the remarkably high bond strength of 9.5 tons per square inch as compared with 5.8 tons per square inch when the steel rod and attached alloy were of the same diameter (Table 63).

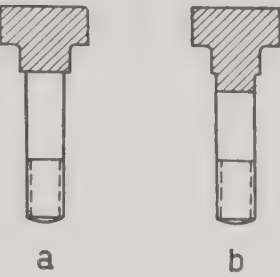


Fig. 160. Composite for bond testing. Tensile specimens, with cross-section of white-metal (A) greater than, and (B) equal to, that of steel.

PRYTHERCH found that temperatures of 350° C, or higher, in the bath of molten tin in which the shells were pre-tinned, were necessary in order

TABLE 63

Type of Specimen	T °C	Bond strength tons/sq.in.
Rod on cylinder of larger diameter	20	9.5
	50	7.7
	100	5.5
	150	3.8
Rod on cylinder of same diameter	20	5.8
	100	4.8
	100	3.6
	200	2.3

References p. 462

to obtain the strongest bond and the dipping time requisite was only 15 seconds; on the other hand at 300° C, as much as 30 minutes dipping time was needed to obtain the best bonds. Tests with a variety of surface finishes on the steel, namely, fine metallurgical finish, fine machined finish, coarse machined finish and second-cut file finish, showed that the surface finish was practically without influence on the adhesion.

(ii) *Thickness*

The influence of the thickness of the free-tin portion of the coating appeared to be also negligible, for specimens with obviously thick coatings were not different from those with thin coatings; the excess of tin merged harmlessly with the bearing alloy in these cases.

(iii) *Influence of Flux Type*

The effects of four active (chloride) fluxes were compared but no differences in adhesion were detected; the fluxes were: (i) fused zinc chloride at 300° C, (ii) fused zinc chloride-ammonium chloride (eutect mixture) at 300° C, (iii) 50 per cent. zinc chloride aqueous solution applied cold, and (iv) cold stannic bromide.

(iv) *Influence of Cooling Time*

The time of cooling was important and the best bonds were those which were quickly cooled. Cooling from 500° C in 15 seconds gave bond strengths of 8.9 tons per square inch, and from 350° C gave 8.8 tons per square inch, but with cooling time protracted to 1 minute 45 seconds the corresponding figures were 7.5 and 7.0 tons per square inch.

(v) *Influence of Tinning Medium*

Prytherch also investigated the effects of various tinning media on bond strength with the following results:

(a) Chempur tin : 9.0 tons/sq. inch.

(b) the anti-friction alloy used for the subsequent lining : 8.2 tons per sq. inch.

(c) 50 : 50 tin-lead solder : 8.5 tons per sq.inch.

(d) cadmium electroplate : 6.3. tons per sq.inch.

The tests were made at 15° C. It is seen that the pure tin is easily the strongest

bond, with the anti-friction metal itself as second best; the values obtained with the tin-lead solder and the cadmium were much more erratic.

When the end of the rod was not tinned prior to pouring the anti-friction alloy but merely brushed with flux, the adhesion was only 7.0 tons per sq.inch, as compared with the 9.0 tons per sq.inch with the pure tin coated ends.

§ 10. THE EFFECT OF THE RATE OF COOLING ON THE ADHESION

The cooling period after soldering may be divided into three parts:

- (i) from soldering temperature to the liquidus of the solder
- (ii) from liquidus to solidus
- (iii) from solidus down to room temperature.

(i) During the first portion of the cooling time the reaction between the tin and the basis metal continues with the formation of compound. The compounds, such as FeSn_2 and Cu_6Sn_5 have melting points much above the normal soldering or tinning temperatures, and, therefore, as they form beyond the capacity of the molten tin to hold them in solution, they separate as crystals and deposit at the interface between the solder and the metal base. Growth of these crystals is slow in the case of the tin-iron compound, as HOARE found¹⁷, and when soldering is carried out expeditiously they are of small size and they do not appreciably embrittle the bond¹³. When, however, the temperature is maintained in this region for some minutes there may be a very decided thickening of the layer of compound and a coarsening of the crystal size with noticeable loss of resistance to shock, so that in the event of fracture, this occurs in the crystalline compound layer. In the case of joints between copper or brass members, the growth of the compounds is much more rapid and the embrittling effect is therefore apparent much more quickly.

(ii) During the second portion of the cooling period, the highest melting constituents in the solder crystallise first at the bond, since cooling begins always on the outside. Provided that the joints are thin, the separation of these high melting constituents, which are rich in lead, is not important because the cooling occurs too quickly, but when the joint has been made on a massive piece of metal which holds the heat well, the segregation may develop until there remains insufficient of the remaining liquid eutectic material to fill the spaces or voids which thermal contraction of the coarser crystals produces, and, at the same time, to fill the middle space in the joint. The consequence in this case is that voids may arise in that space and cause unsound joints which fail under test in the incomplete solder layer²⁷.

(iii) During the third stage, in the total absence of a liquid phase, the rate of reaction and of compound formation is very much slower and the effect due to diffusion is, in the few seconds normally required for the making of a joint, too slow to have any pronounced effect. The most important factor during this period is the disparity in the coefficients of thermal contraction of the solder and the basis metal. The coefficient in the case of pure tin is 24×10^{-6} ; for 60/40 tin-lead solder it is 27×10^{-6} ; for 30/70 tin-lead solder it is 29×10^{-6} ; for pure lead it is 31×10^{-6} . In the cooling range of solders, the corresponding coefficient for mild steel is only 11×10^{-6} , for copper it is 16×10^{-6} , and for common brass it is 20×10^{-6} .

It is plain, therefore, that great stresses may arise due to these differences in the contraction of the solder and the metal of the joint unless they can be relieved simultaneously by creep in the solder²⁵. The creep strength of tin-lead solder is low, especially immediately below the solidus, and there is plastic flow until the stress is negligible. In solders containing a small percentage of antimony, the antimonial solders of commerce, for example, the creep strength is considerably higher and the risk of failure during cooling of copper, and particularly brass, parts is often serious²². The risk to joints upon brass or zinc surfaces is considerable even with the tin-lead solders because of the presence in these joints of crystals which are much more coarse than in zinc-free joints. When antimony is present in the solder used for brass or zinc-containing surfaces, the risk of failure is increased by the coarsely crystalline compound formed between the antimony and the zinc. Failures of this type occurring during the final stage of cooling are termed "hot-short".

Similar considerations apply in the case of anti-friction alloys bonded to steel shells; the stronger the alloy and more resistant to creep, the greater the stress and the liability to fail during cooling. PELL-WALPOLE mentions²⁷ that alloys hardened with cadmium were liable to crack away from the shells during cooling, while alloys free from cadmium were cooled at the same rate without danger of cracking.

§ 11. STRENGTH OF SOLDERS AND OF SOLDERED JOINTS

(a) *Solders in Bar Form*

The strength of solders in bar form is related to the cohesion in the solders but affords no indication of their adhesion to metals. NIGHTINGALE and HUDSON²⁵ gave figures for the strength of solders in bar form and also for

the strength of joints made with these solders on copper brass and mild steel. In order to show the influence of antimony figures are given (Table 64)

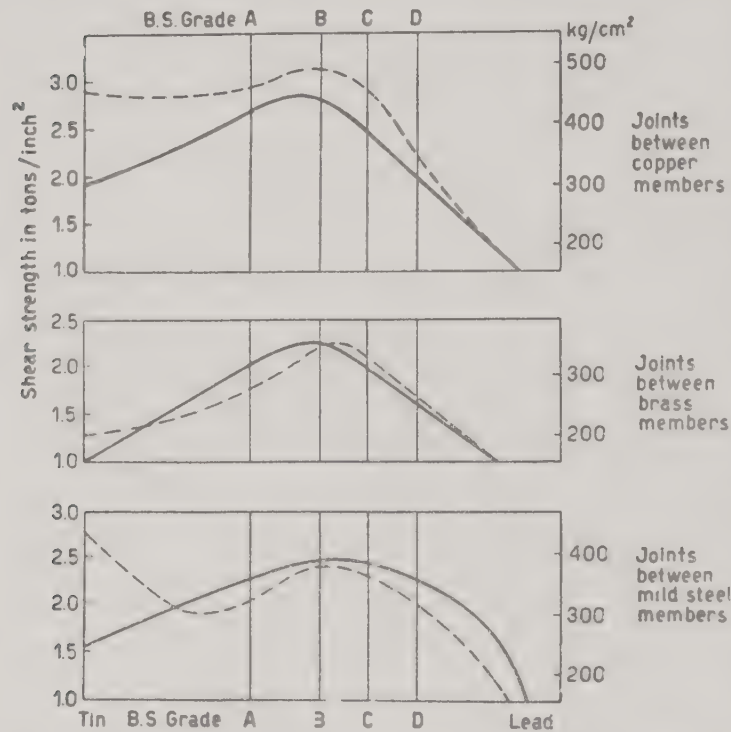


Fig. 161. The effect of solder composition on the shear strength of soldered joints. Full line, tin-lead; dotted line, antimonial.

for a range of solders in which six per cent. of tin was substituted by antimony, this amount being just within the solubility of this element in tin. The non-antimonial solders were made from pure tin and pure lead and were consequently more ductile than commercial solders would have been (Fig. 161, 162).

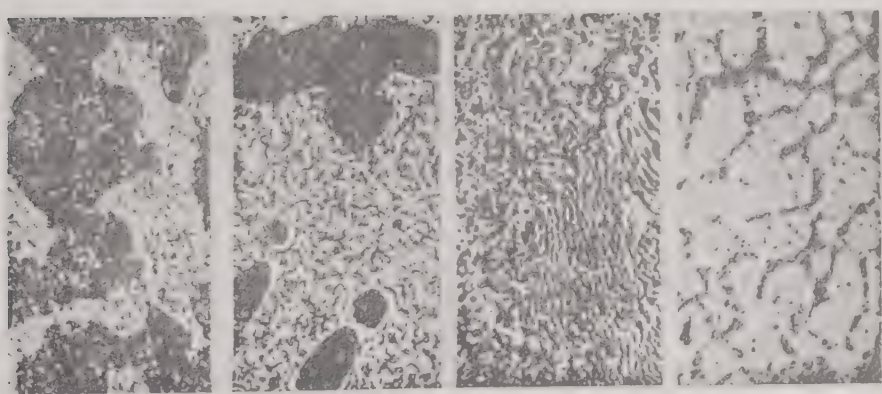
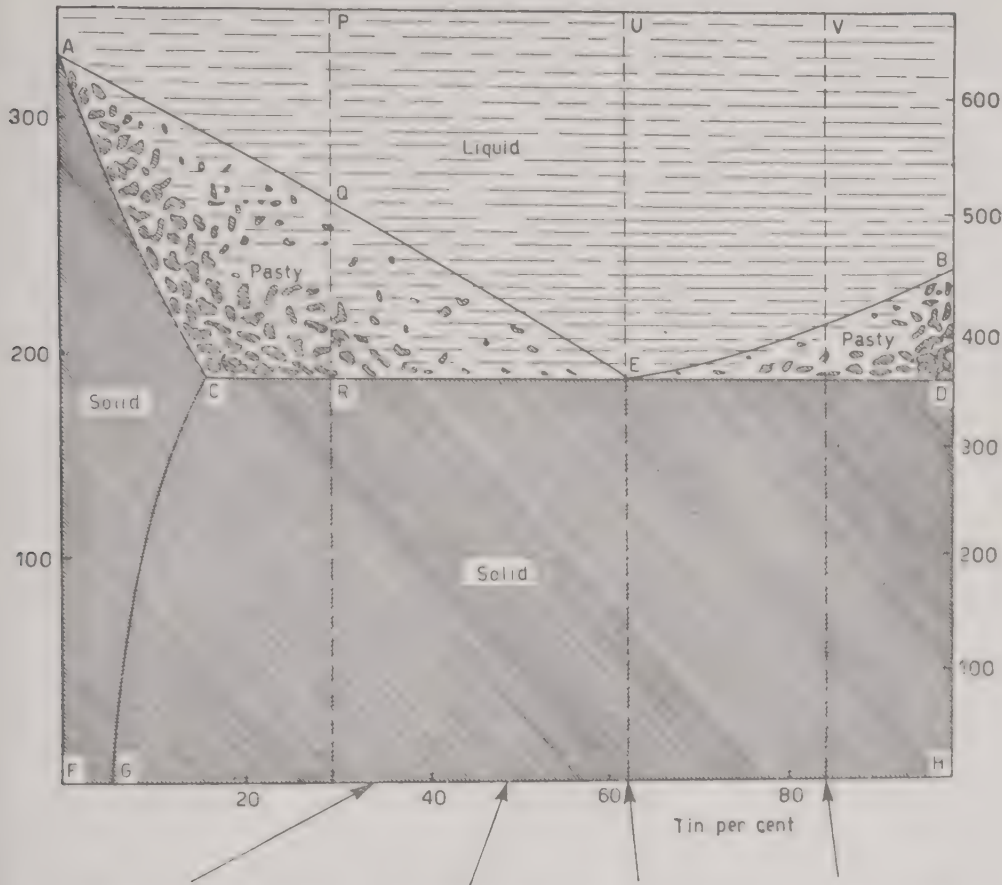
(b) *Strength of Soldered Joints in Tinplate*

MCKEOWN²² gives results of tests of the strength of lap joints

TABLE 64
INFLUENCE OF ANTIMONY ON STRENGTH OF JOINTS
(Values in Tons per sq. inch)

per cent.		Bar solder		Shear strength of soldered joints on		
Tin	Anty:	Tensile	Shear	Copper	Brass	Mild Steel
100	—	0.94	1.28	1.90	1.05	1.58
94.5	5.6	2.81	2.86	2.99	1.31	2.80
66.1	—	3.43	2.77	2.82	1.39	2.42
59.4	3.6	4.42	3.07	2.73	1.39	2.16
56.1	—	2.95	2.79	2.49	2.23	1.98
50.2	3.0	3.75	3.06	3.02	2.20	2.38
44.8	—	2.65	2.33	2.68	2.07	2.49
40.0	2.45	3.55	2.64	3.02	2.11	1.78
33.7	—	2.87	2.13	2.05	1.67	2.33
30.1	1.75	3.29	2.19	2.34	1.67	2.01

References p. 462



(a) (b) (c) (d)

Fig. 162. Top: Constitutional diagram of the tin-lead alloys. Bottom: Photomicrographs of various solders. The black areas in (a) and (b) show lead embedded in eutectic solder; (c) is entirely eutectic and (d) shows eutectic as darker material embedded in pure tin.

when pulled in a tensile-testing machine in which the rate of movement of the head, that is the rate of extension, was 0.5 inches per minute. For thin material such as tinplate of 0.011 inch thickness or copper and brass strips of 0.036

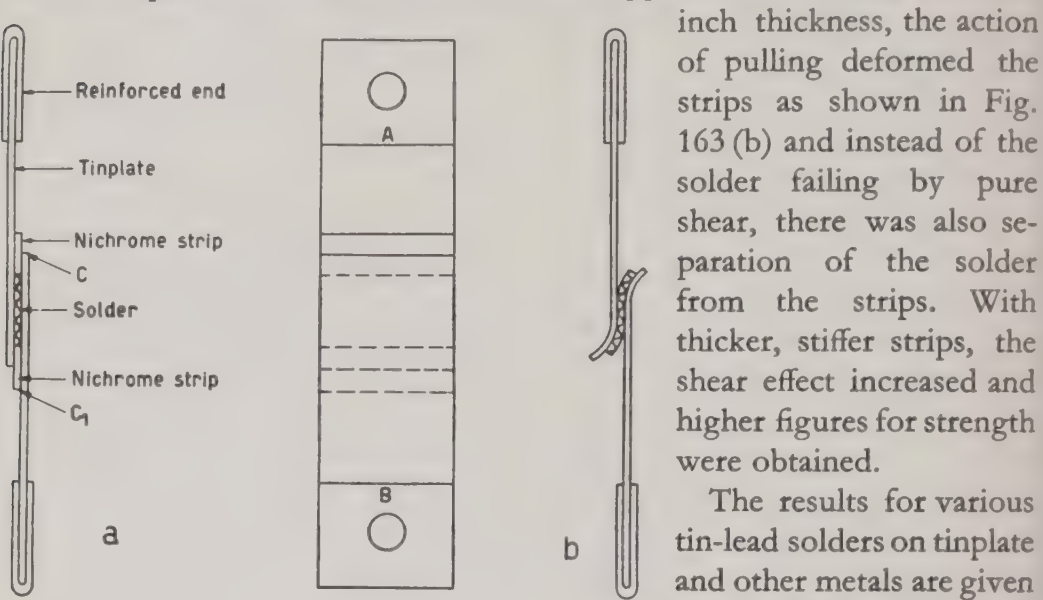


Fig. 163. Tensile Test for Lap Joints
(Mc KEOWN).

inch thickness, the action of pulling deformed the strips as shown in Fig. 163 (b) and instead of the solder failing by pure shear, there was also separation of the solder from the strips. With thicker, stiffer strips, the shear effect increased and higher figures for strength were obtained.

The results for various tin-lead solders on tinplate and other metals are given in Table 65.

TABLE 65
TIN-LEAD SOLDERS ON TINPLATE 0.011 inch
Breaking loads in lb.

	Percentage of Tin					
	100	63	50	40	30	20
Tinplate (0.011'')	290	325	315	320	295	265
Copper (0.036'')	300	340	342	342	335	280
Brass B.S.S. 265 (0.036'')	—	—	360	385	380	—
Brass B.S.S. 267(0.036'')	—	—	405	405	400	—

(c) Creep Strength of Soldered Joints

The maximum load which a soldered joint can sustain indefinitely is much less than that which is necessary to cause immediate failure. Investigations of creep failures in soldered joints have been made by GONSER and HEATH, by BAKER and by McKEOWN²², and it is established that a stress of only a few hundred pounds applied for a month or less will cause failures. These failures occur in the solder between the alloy layers, not in the alloy layers

References p. 462

themselves, and they indicate nothing therefore about the shear resistance of the bonding layers or the strength of the adhesion between the solder and the basis metal, except that it is greater than the creep strength of the solder itself.

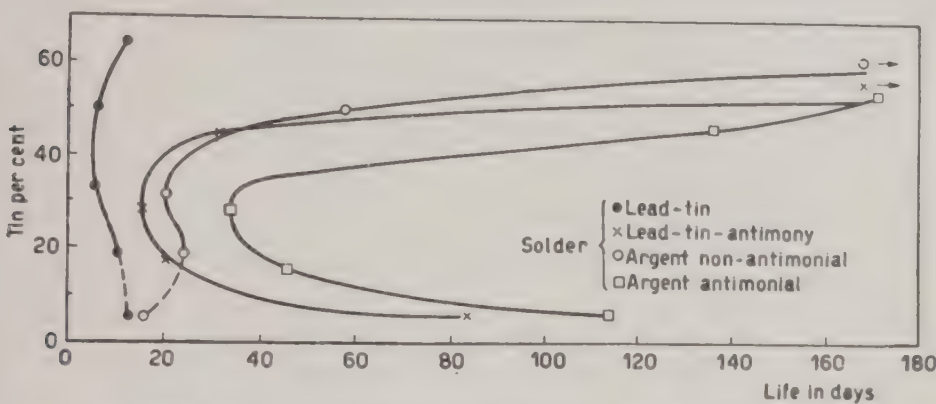


Fig. 164. Life tests on lap joints in tinplate at 700 lb/in² at 20° C.

Fig. 164, due to McKEOWN, shows curves of life tests on lap joints in tinplate maintained for the periods stated under a steady load of 700 lb per square inch. Fig. 165 shows the breaking stress on similar joints in stepped loading tests. In these tests, an initial load of 700 lb. per square inch was applied and each day increased by 20 lb. until fracture occurred. The superiority of the eutectic solders is evident. Fig. 166 shows the results obtained at 100° C to be considerably lower.

BAKER¹ found creep values of joints in steel to be lower than in copper and much lower than in brass; failures all occurred in the solder and the differences are attributed to the absence of appreciable alloy formation in

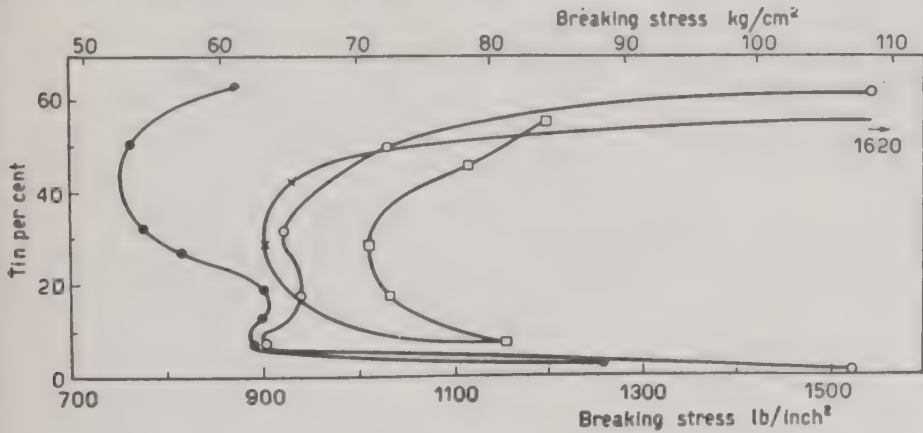


Fig. 165. Stepped loading tests on lap joints in tinplate at 20° C.

the first case as compared with the copper and the brass. The thickness of the joints in both BAKER's and MCKEOWN's tests, 0.006 inches and 0.008 inches respectively, was greater than is usually recommended for practical purposes, namely, 0.003 to 0.005 inches. This fact favours creep in the solder layer, for in thinner joints there would be greater contamination of the solder layer by the basis metals.

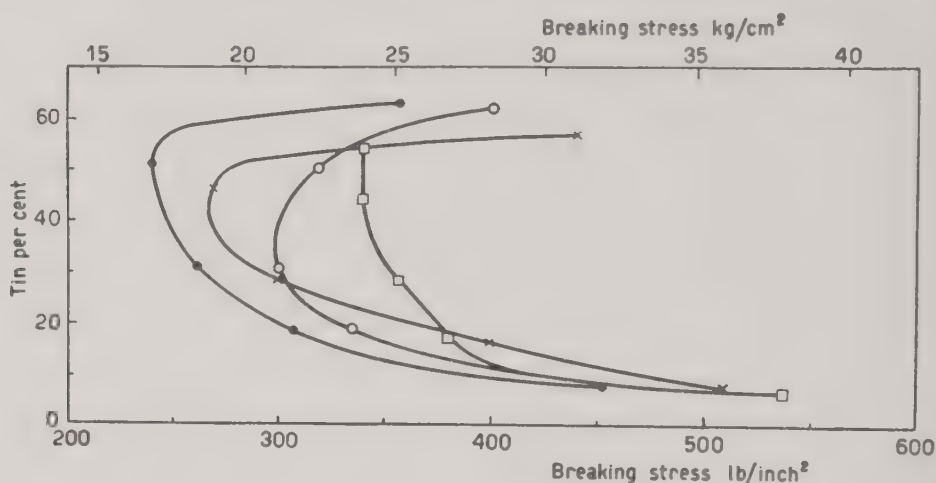


Fig. 166. Stepped loading tests on lap joints in tinplate at 100° C.

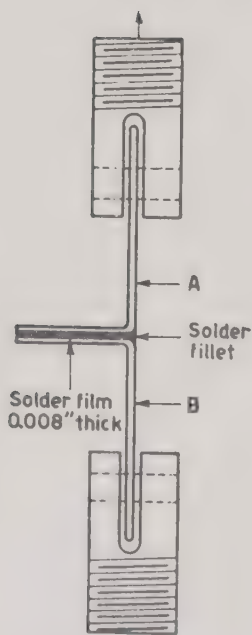


Fig. 167. Diagram of CHADWICK Tearing Test of Soldered Joints.

References p. 462

CHADWICK⁴ devised a tearing test for solders (Fig. 167). Two inch-wide strips of tinplate were bent at right angles, placed "back to back" with one side touching and were then soldered with the flux and solder, under investigation. The free ends of this "T"-shaped specimen, (that is, the horizontal cross-bar of the "T") were then pulled apart slowly. When the adhesion to the two strips was equal, the solder was torn through its middle layer and half of it was left on each strip. This was the case with solders of very low tin content, less than 20 per cent. When the solders contained more tin than this, the solder detached from one surface of tinplate and was left almost entirely upon the other surface. The stiffening of the thin tinplate strip in this way caused this strip to bend to a much larger radius of curvature than the other and the joint had the shape shown in Fig. 168. From this fact it is

apparent that the stiffness of the strips has much influence on the results obtainable in such a test. Further, it is obvious that if perfectly rigid strips were used, they could not bend and the strength of the whole soldered section would come into play. If we assume that the strips have no stiffness at all of their own before being soldered, we must expect that the formation on them of tin-metal compound crystals must impart some stiffness which must increase as the amount of compound grows at soldering temperature. Apart from this stiffness due to the compound, there is only the force of adhesion at each surface and of cohesion in the solder between to be overcome, but as any force applied is resisted only by a single layer of atoms at any instant no measurable force will be required to separate them. On the face of it, therefore, the test can tell us nothing about the strength of adhesion of solder to a soldered surface. Nevertheless, by standardising on metal strips of con-



sistent thickness and stiffness and other characteristics, it is possible to demonstrate a relationship between the “steady tearing load” per inch of width and the composition of the solders. Results of tests by McKEOWN are shown grafically in Fig. 169.

Fig. 169. Behavior of solders rich in tin during CHADWICK tearing test.

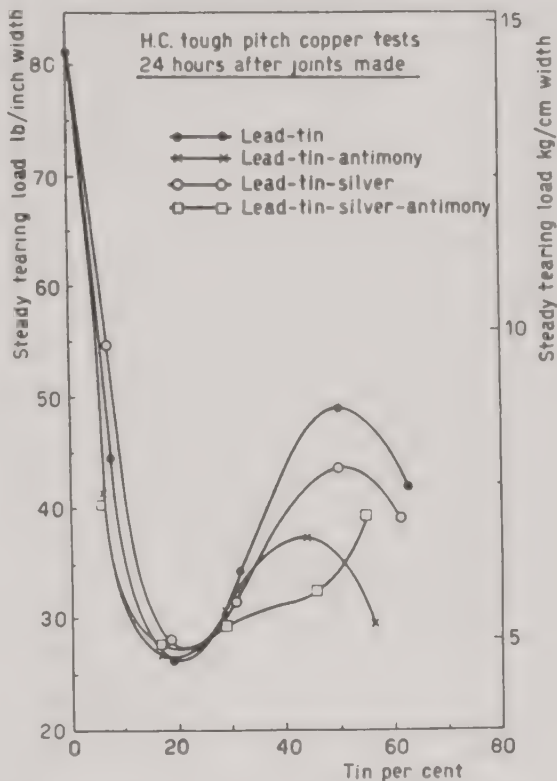


Fig. 168. Tests on CHADWICK-type joints in copper, 0.018 in. thick.

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CHAPTER 9

THE PHYSICAL TESTING OF ADHESION AND ADHESIVES

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§ 1. THE SIGNIFICANCE OF TESTS

Physical tests of adhesives are of two kinds—(1) “End-use” tests in which an attempt is made to assess the performance of the adhesive by inspecting and testing representative joints previously subjected to some scheduled treatment which may be, for instance, conditioning at room temperature or exposure to the weather for months or years; (2) “Production control” tests intended to assess the uniformity of the characteristics of the adhesive. “End-use” tests are described in § 2 and § 3 of this chapter and “Production control” tests in § 4.

It is the author's experience that the value and significance of any test can easily be over-emphasized; great care should be taken in drawing sweeping conclusions from the results of a laboratory test. Thus if adhesives are placed in order of merit according to their performance in a lap joint test, it will be found that the order of merit may be quite different when determined by a peeling test. A test is an abstraction from reality in which the relation between two variables is singled out for examination, and while almost a truism it is sometimes forgotten that there are many factors (not all of which are yet amenable to precise laboratory testing) that must be taken into account in arriving at a true overall estimation of the value of an adhesive.

It is perhaps hardly necessary to emphasize that the results of a single determination are usually of little significance. However carefully a measurement is planned and executed it is impossible to keep control of unwanted variables. Hence all test results are subject to error. In so far as these errors are of a random as distinct from a constant character they can be reduced by repetition of the tests and taking a mean value, and wherever possible “control” tests should be made. Thus if it is desired to examine the resistance of joints to boiling water it is advisable to test some

of the joints before immersion in boiling water to ensure that no mistakes have been made in, for example, the mixing of the glue. If, as in most tests to destruction, the scatter is considerable, then a more comprehensive statistical analysis can be very helpful in arriving at the probable truth. But the methods of statistical analysis do not relieve the experimenter from the responsibility of weeding out results that he knows to be wrong, and in the words of Sir HARRY RICARDO¹, "Before you accept the reading of any instrument, put it through the following test, 'Is it probable, is it reasonable, and does it accord with your common sense?'"

The methods of statistical analysis constitute a specialised study outside the scope of this book and the purpose of this note is to review briefly what has been done in their application to tests of the strength of glued joints.

Histograms of strength of plywood joints have been published by BITTNER² and of joints made with assembly glues by Aero Research

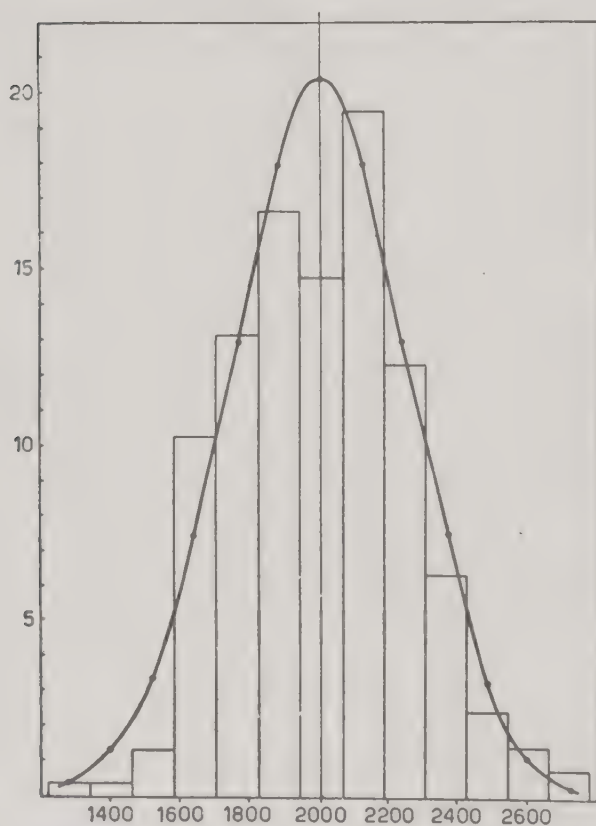


Fig. 170. Histogram showing distribution of shear tests on "Araldite".

205 tests of joints made with "Araldite" Type 1 using lap joints of 20

Limited³. These indicate that the distribution is a normal one but in so far as nearly all the fractures take place in the wood in such tests if suitable synthetic adhesives are used, the effect of variations in glue quality are slight though sometimes statistically significant. Thus with urea-formaldehyde resin and hardener a significant and positive correlation was found between the strength of joints tested dry and wet; *i.e.* a glue and hardener giving strong wet joints usually gave strong dry joints and vice versa. Tests of metal-to-metal joints give more precise information as it is possible using suitable metals of sufficient thickness to ensure rupture in the adhesive. Fig.

s.w.g. strips 1 inch wide with $\frac{1}{2}$ inch overlap in aluminium alloy to specification D.T.D. 610B.

An important application of statistical analysis is to determine the minimum number (n) of tests required to establish significant differences between means (*e.g.* between means of control samples and of treated samples.) Thus for a coefficient of variation of 15% as shown by the above tests of "Araldite" and assuming a 1 in 20 level of statistical significance, we can derive the following table ⁴:

Difference between means of:	Minimum number of tests
5%	72
10%	18
20%	7

This table shows, for instance, that if the means of the control and experimental tests respectively differ only 5% from the mean of all the tests, then this difference can only be regarded as significant if at least 72 experimental and 72 control tests have been made.

In the use of metal-to-metal adhesives in aircraft construction statistical analysis in the form of "Quality control" is of value in inspection and in maintaining a high standard.

§ 2. TESTS OF JOINT STRENGTH

(a) *Tension Tests*

At first sight the fundamental as well as the simplest test of the strength of a joint would seem to be a tensile test in which the two adherends, for example in the form of rods, are cemented together end to end and then pulled apart by a tensile force along their common axis.

Unfortunately the stress distribution at the interfaces and in the adhesive will only be uniform in the special case where both adhesive and adherends have an equal lateral contraction under tensile strain. In the elastic region this means that adhesive and adherends must possess the same values of elastic constants, and in practice this will never occur.

The non-uniformity of stress distribution in such tensile tests manifests itself in various ways. It can be clearly demonstrated photoelastically and is probably the main cause of the change in breaking load that occurs as the thickness of the adhesive is varied, as shown in Fig. 171 ^{5, 6, 7}

Usually the adherend contracts laterally much less than the adhesive but since the adhesive is firmly anchored to the adherends its lateral deformation will be restrained^{8,9}. This restraint will be most effective at the adhesive-adherend interface and will decrease as the distance from the interface increases.

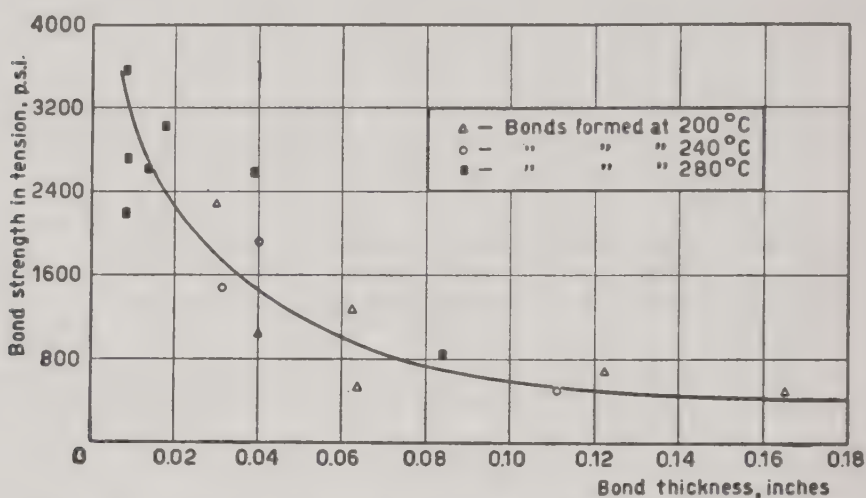


Fig. 171. Variation of tensile strength with thickness of adhesive.]

A test approximating to a tensile test has been used in Germany. It was devised by RUDELOFF¹⁰ and consists in forcing apart two thick pieces of wood glued crosswise edge to edge as shown in Fig. 172.

The Forest Products Laboratories of Canada have recommended a tension test for plywood in which the load is applied through maple blocks previously cold-glued to a piece of plywood 1" by 1" in area¹¹.

The A.S.T.M. have a standard D897-49 for tensile tests on adhesives for wood and metal using test grips and adherends of the shape shown in Fig. 173. A somewhat similar type of test for vulcanised rubber to metal is described in A.S.T.M. D429-39; A.S.T.M. D952-48T describes a test

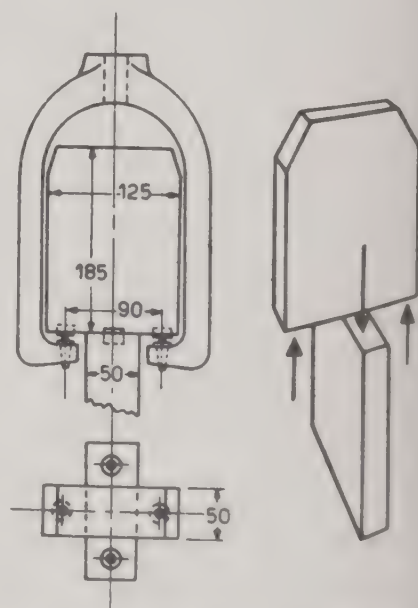


Fig. 172. RUDELOFF's tensile test for wood joints.

of bond strength of laminated plastics by applying a tensile force to a specimen glued with "Redux" between two metal blocks. SCHMIDT^{12, 13} has proposed a test of paint adhesion in which a small block of wood is cemented to the paint film and the force required to pull off the block is then measured. A test has been proposed for measuring the strength of

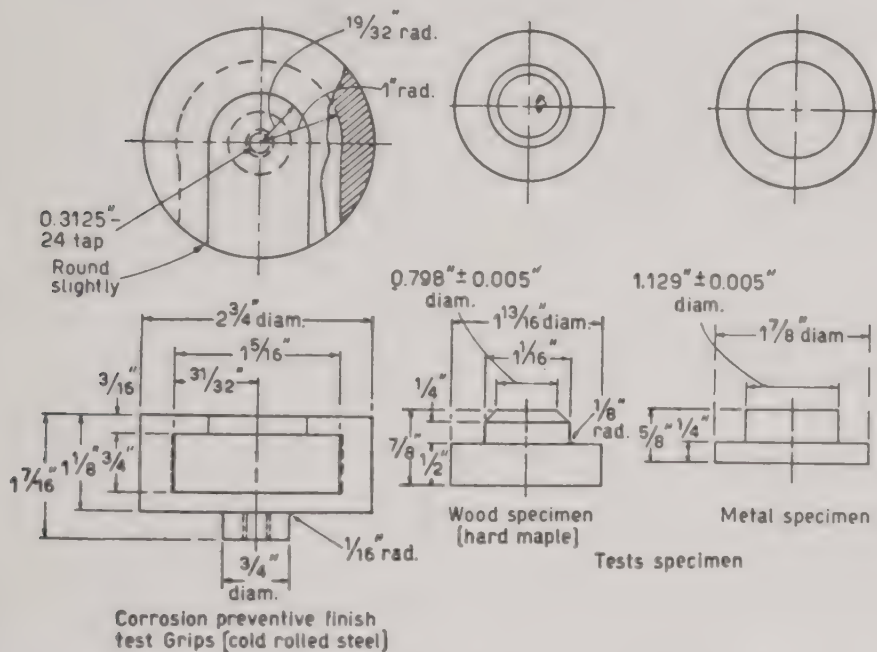


Fig. 173. A.S.T.M. tensile test for wood and metal joints.

Note.—Surfaces of metal specimens shall be ground flat and parallel. It is preferable to grind all metal specimens at the same time.

electro-deposited coatings¹⁴ in which a lug is soldered to the plating; unfortunately the heat produced in the soldering alters the strength of the bond between the plating and the base metal; possibly the use of a modern synthetic adhesive would be more satisfactory.

Wax pick tests are used for assessing coated papers¹⁵.

MOSES and WITT¹⁶ have tested the adhesion of films to adherends by inertia tensile forces due to ultrasonic vibration producing accelerations exceeding 200,000 times that of gravity.

(b) Shear Tests

A variety of tests have been devised in which the forces applied tend to make the adherends slide apart; while it is possible, as described below, to apply a pure uniform shear to a joint, nearly all the tests at present used

give rise to a non-uniform shear stress generally accompanied by forces at right angles to the plane of the adhesive.

(i) *Lap joints under tensile load*

A very common test of an adhesive is to pull apart two pieces of wood joined by a lap joint. BS 1204: 1945 describes the types of lap joint, made of slips of $\frac{1}{8}$ inch thick beech veneer, for testing close contact and gap joints respectively. The dimensions are shown in Fig. 174. The purpose of the gap joint is to assess the performance of thick layers of adhesive such as frequently occur in practice. Full details of conditioning in air and in water

and of testing are given in BS 1204: 1945.

Similar tests of metal-to-metal adhesives are described in DTD 775 specifying lap joints 1 inch wide with a 1 inch overlap in 20 s.w.g. "Alclad".

Adhesives for plywood are tested with a specimen having a three ply structure in which the grain of the centre veneer crosses that of the two outer veneers. American, British and French test specimens are shown in Fig. 175. The behaviour of these specimens under load is demonstrated in Fig. 176¹⁷ (see also Chapter 4, § 9, for the mechanism of the failure). It would appear that the influence of jaw constraint might be appreciable in the American specimen in view of its comparatively short length.

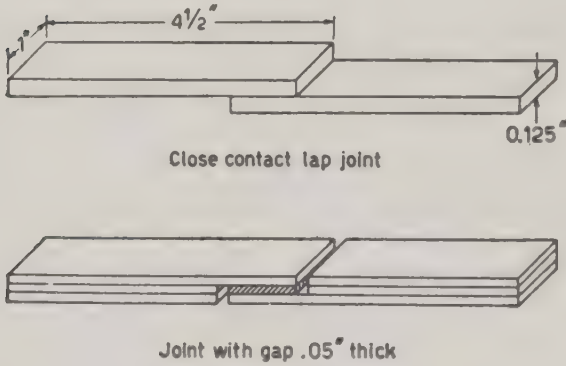


Fig. 174. Close contact and gap joints according to B.S. 1204.

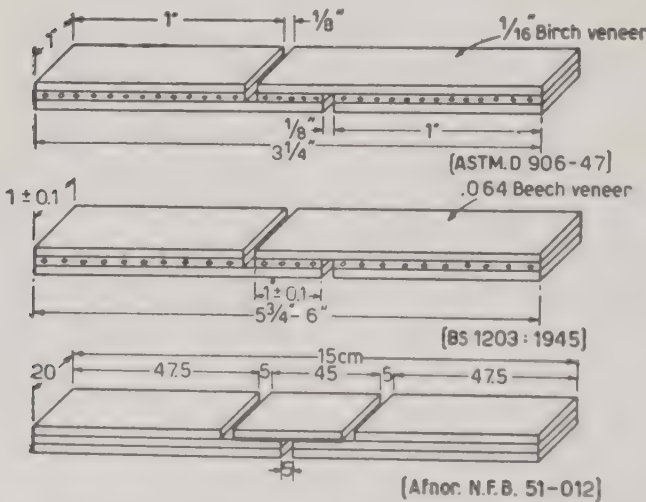


Fig. 175. Plywood adhesive test joints used in U.S.A., England and France.

The results of tests of the adhesion between the veneers of factory made plywood will depend upon the thickness and number of plies.

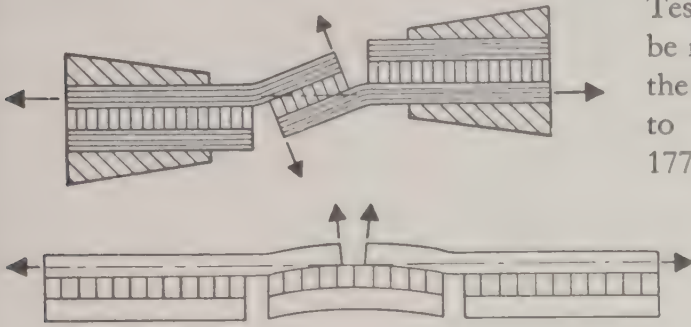
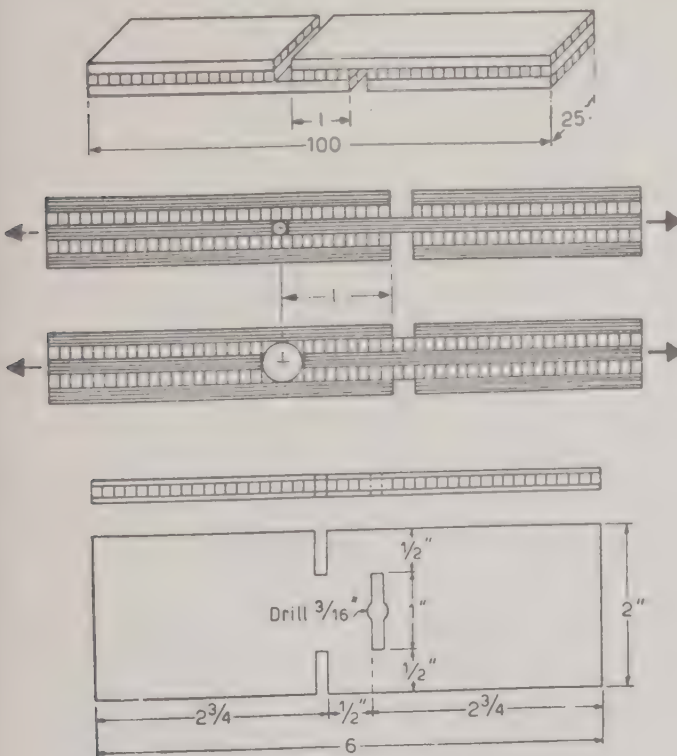


Fig. 176. Deformation of plywood adhesive test joints. Above American and British test specimen; below French test specimen.

measuring the force required to pull a single cord in direction of its axis from a strip of rubber in which one end of the cord over a given length is embedded. Thus the quantity measured is a shearing force acting across the cord to rubber surface. (Study of the H Test for Evaluating the Adhesive Properties of Tire Cord in Natural and G.R.S. Rubbers¹⁸).



The adhesion of gummed tape is frequently measured by an apparatus originally devised by McLaurin¹⁹ and modified by Harnden²⁰. The procedure is described in T.A.P.P.I. Tentative Standard T463 m-43²¹. The gummed tape is subjected to a strain simulating that produced when the two flaps of a corrugated board box after sealing endeavour to spring back into the open position.

Fig. 177. Tests of adhesion in plywood.

HOEKSTRA and FRITZIUS²² have devised a test of the shearing strength of a paint film applied to the upper surface of the three pieces of metal shown in Fig. 178 while they are rigidly clamped together by the screws. The

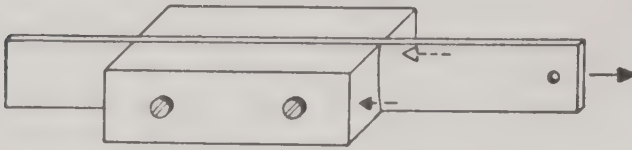


Fig. 178. Shear test of paint film devised by HOEKSTRA and FRITZIUS

The film is tested by removing the screws and applying loads tending to slide the central strip from between the two outer blocks.

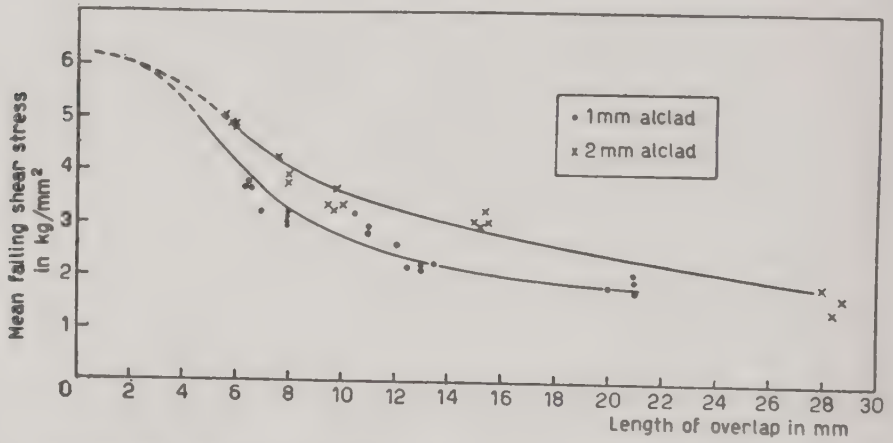


Fig. 179. Variation of apparent shear stress with overlap for 1 mm and 2 mm sheet. Tests on simple lap joints of "Alclad" made with "Redux" (Nationaal Luchtvaart Laboratorium, Amsterdam, Report No. M 1275, Fig. 11, 1948).

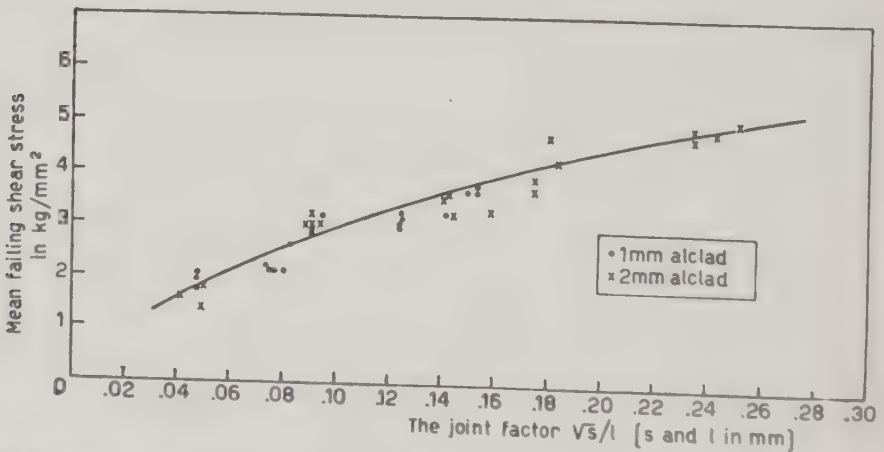


Fig. 180. Apparent shear stress plotted against joint factor. Tests on simple lap joints of "Alclad" made with "Redux" Nationaal Luchtvaart Laboratorium, Amsterdam, Report No. M 1275, Fig. 15, 1948).

(ii) *The joint factor*

In all tensile shear tests the thickness of the adherends, as well as the overlap, influences the apparent shear stress at rupture. For a given glue and given adherends the author has found it useful to plot the apparent shear stress at rupture against a parameter called the "joint factor" (see Chapter 4) which is the square root of the thickness of the adherend divided by the overlap. In this way one curve will suffice to cover a whole range of tests; Figs. 179 and 180 illustrate the utility of the joint factor²³.

(iii) *Lap joints under compressive load*

A.S.T.M. Standard D905-49 specifies a shearing test for wood under compressive load in a special jig as shown in Fig. 181. This test was

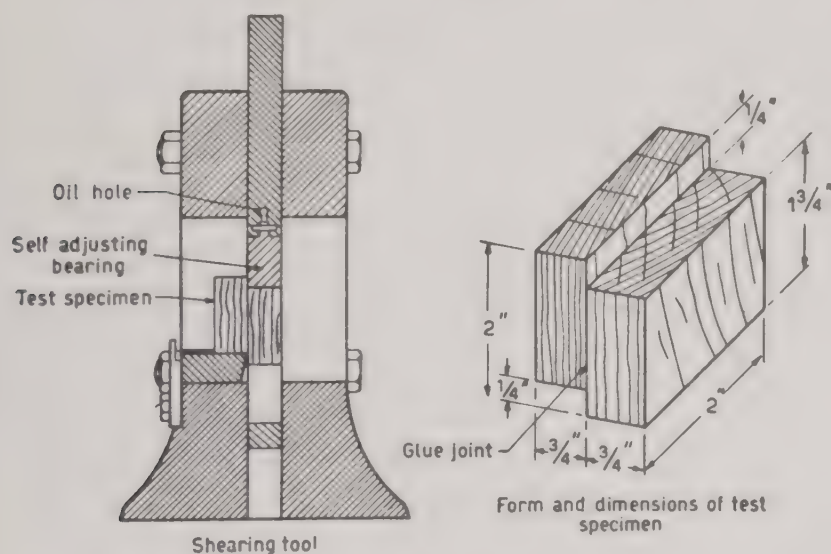


Fig. 181. Block shear test used in U.S.A.

developed by the U.S. Forest Products Laboratory and is in principle similar to that described by BAUSCHINGER in 1884²⁴. Owing to the thickness of the wood specimens this test does not lend itself to tests of the water resistance of the adhesive. A modified form of this test, due to Dr W. D. DOUGLAS, is shown in Fig. 182. It is especially useful in making a "post mortem" examination such as is necessary for example in determining the effectiveness of radio heating in a thick laminated assembly. The test specimens can be cut out from the assembly where desired.

The effect of variation in the grain direction of the test specimen in shear tests has been reported in U.S. Forest Products Laboratory Report ²⁵.

A block shear test used by the Nationaal Luchtvaart Laboratorium

of Amsterdam is shown in Fig. 183.

In block shear tests the tearing stresses are not as large as in tensile lap joint tests. Nevertheless, as is shown in Chapter 4 distribution of shear stress on a typical test specimen is far from uniform.

For testing solder the British Non Ferrous Metals Research Association have used an annular compressive shear test. It consists of an outer ring into which is soldered a concentric cylindrical plug ²⁶; an axial compressive load is applied and shears the soldered joint.

(iv) Scarfed joints

The scarfed joint, in view of the more uniform stress distribution obtained, would seem to be a better test specimen than the plain lapped joint. It is on the other hand less easy to make and perhaps less representative of practical conditions.

In the scarfed joint the adhesive is subjected to shear parallel to the

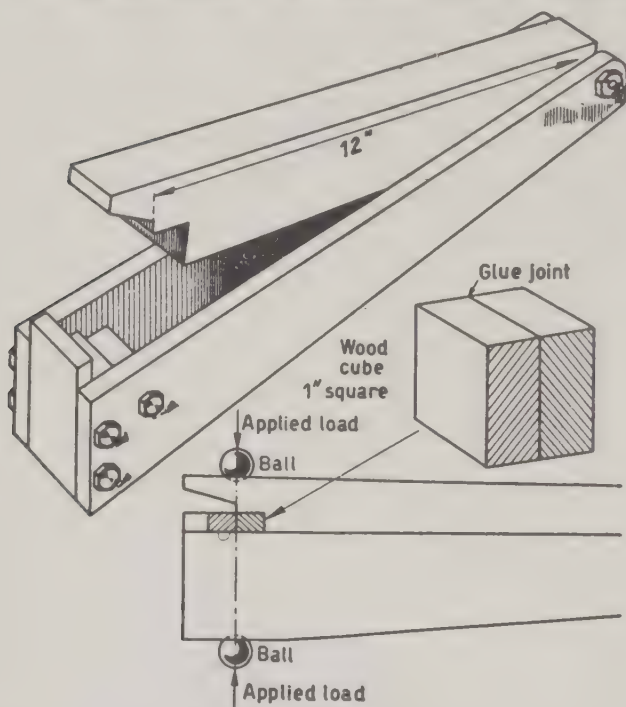


Fig. 182. Block shear test devised by Dr W. D. DOUGLAS. The nutcracker device shown is useful for making shear tests on joints between two half cubes making a cube one inch square.

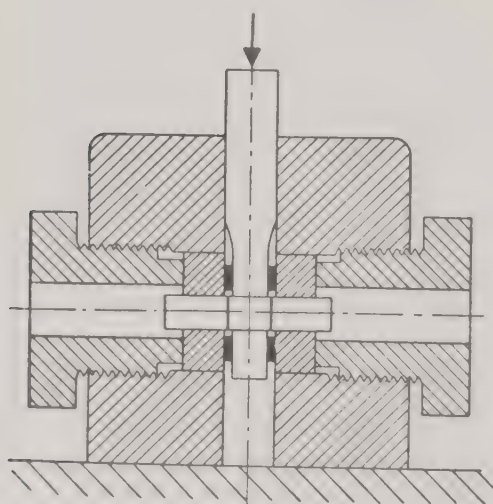


Fig. 183. Shear test used by Nationaal Luchtvaart Laboratorium, Amsterdam.

$$\tan \alpha = \sigma_m / \tau_s$$

• Redux
 ○ Araldite
 x Pliobond

$\tan \alpha = \text{ratio of } \sigma \text{ in the glue}$
 I Shear stress in the glue; redux
 II " " " " " " araldite
 III Tensile " " " " " " redux
 IV " " " " " " araldite

τ kg/mm²
 σ kg/mm² (in the glue)

Compression $\tan \alpha$ ← → $\tan \alpha$ tension

Figure 1 consists of two graphs showing the dependence of the critical stress σ_c on the angle of compression $\tan \alpha$ for three materials: Redux, Araldite, and Plibond.

The left graph plots σ_c (kg/mm²) on the y-axis (ranging from 0 to 25) against $\tan \alpha$ on the x-axis (ranging from -1.5 to 0). The curves show a minimum value of σ_c around $\tan \alpha = -1.0$. The data points are marked with dots for Redux, crosses for Araldite, and squares for Plibond.

The right graph plots σ_c (kg/mm²) on the y-axis (ranging from 0 to 25) against $\tan \alpha$ on the x-axis (ranging from 0 to 2). The curves show a decreasing trend of σ_c as $\tan \alpha$ increases. The data points are marked with dots for Redux, crosses for Araldite, and squares for Plibond.

Legend:

- Redux
- × Araldite
- Plibond

References p. 491

from a rather crude analysis which neglects the elastic properties of adhesive and adherends.

Results of tests by the National Luchtvaart Laboratorium, Amsterdam, are given in Figs. 184 and 185, and show that the shear stress increases as the tensile stress is reduced or the compressive stress increased²⁷. The shear stress at zero normal stress is about 5 kg/mm² (7000 p.s.i.) for both "Redux" and "Araldite". This limiting stress is of the same order as that found from tests on simple lap joints at a high value of the joint factor;

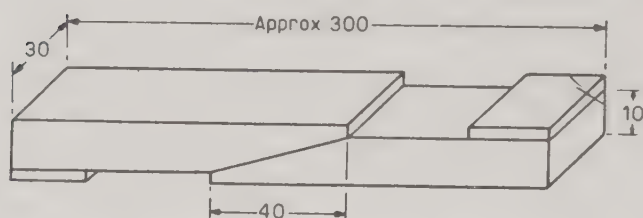


Fig. 186. German scarf joint for wood. DVL test specimen.

they are, however, significantly lower and this may be due the difficulty in making long scarfed joints with the same control over glue thickness and inhomogeneities as is possible in short lap joints.

The scarfed joint has been used in Germany for testing wood glues and Fig. 186 shows the dimensions of the D.V.L. test specimens used for specification tests²⁸. In comparing the results of tests on scarfed joints in wood with tests by other methods the effect of the grain direction should not be overlooked.

(v) Shear by bending

A beam in three point loading under a central load W will be subjected to a vertical shearing force $W/2$ (Fig. 187). The magnitude of the longitudinal

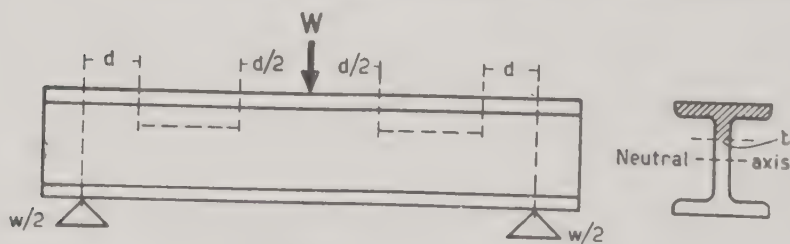


Fig. 187. Production of shear by bending.

(horizontal) shearing stress q and of the equal vertical transverse shear stress, at a point in the section where the boundaries of the section are vertical for some distance, as in the web of an I beam or anywhere in a beam of rectangular section, is given by the elementary BERNOULLI-EULER theory:

$$q = \frac{W A \bar{y}}{2 b I} \quad (\text{see Fig. 187})$$

This type of loading has been used by the E.M.P.A. of Zurich²⁹ for

measuring the shear strength of a glue line at the neutral axis of a beam both for wood and for metal to metal glues.

FROCHT³⁰ has shown that the shear stress is not uniformly distributed as the above elementary formula suggests (but note that his equations 3.36 should all be divided by two). FROCHT made a photoelastic analysis of the shear stress in beams of rectangular cross section under three point loading and found that the elementary theory gives the correct value for the parts of the neutral axis marked by dotted lines in Fig. 187 but that outside these dotted positions the shear stress was less than the value predicted by the elementary formula.

It would appear therefore that the shear strengths derived from this type of test are likely to be higher than the true value and it is perhaps relevant to this that the shear strength of "Araldite" to Anticorodal Bond Avional M was found to be 6.75 kg/mm^2 (9,600 p.s.i.) which is rather higher than the maximum values given by other tests. If appreciable deformation takes place in such a test there will be in effect a shortening of the span of the beam. This has been investigated by WESTWATER³¹.

(vi) Tests in pure shear

While the plain lap joint is widely used and is representative of practical conditions of use, the complicated stress distribution and type of stress imposed make it unsuitable for evaluating the fundamental strength characteristics of adhesive and adherend.

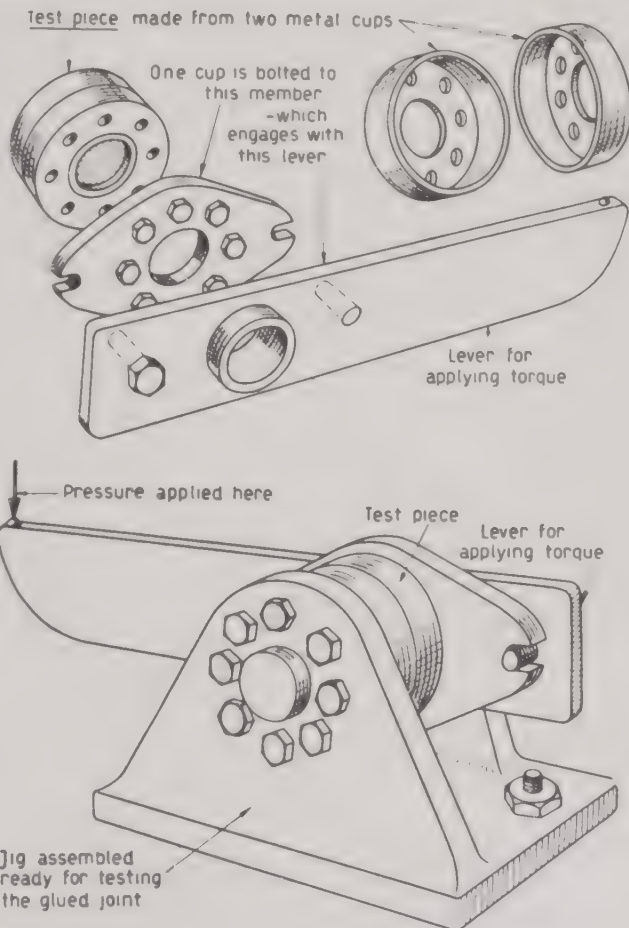


Fig. 188. Production of shear by twisting.

A substantially pure shear stress can be produced by twisting a tube cemented to a concentric tube as shown in Chapter 4, § 2. A sketch of a practical test rig used by the Division of Mechanical Engineering of the National Research Council (Canada) is shown in Fig. 188. The base is bolted to a testing machine arranged for compression tests, a downward load applied to the end of the lever arm produces a torque on the cup-shaped adherends glued together to form a tubular butt joint. The cups are approximately 4 inches in diameter with walls of $\frac{3}{32}$ inch in thickness. Tests with brittle lacquer showed that cracking at 45° appeared to take place simultaneously in a narrow circumferential band divided by the glued joint.

Between mild steel cups "Redux" joints have given a mean failing stress of 7920 p.s.i. in such a test.

(c) Bending Tests

MUHLNBRUCH³² has suggested that a bending test under three point

loading be used to find the flexural rigidity and hence to detect softening and breakdown of the adhesive in multi-ply specimens after soaking in water. The flexural rigidity is a function of the effectiveness of bonding between the veneers.

Fig. 189 shows a German bending test for assessing the quality of wood joints³³.

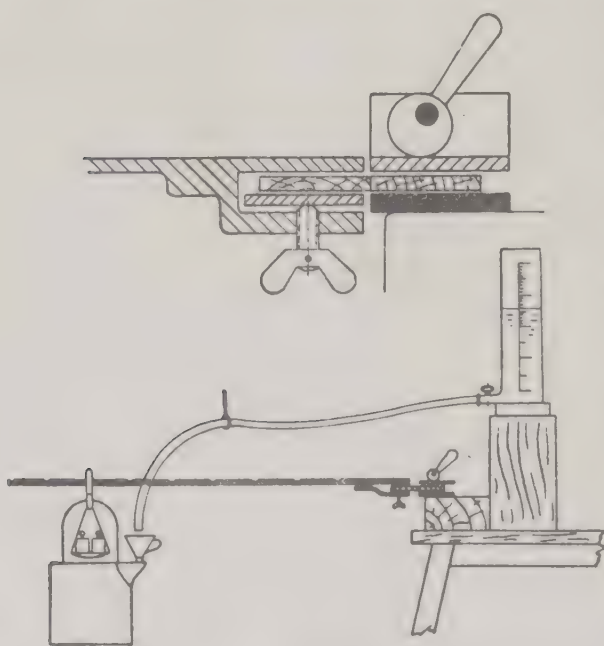


Fig. 189. Improvised German test of joint strength under bending.

(d) Cleavage Tests

The cleavage test may be described as a variant of the tensile test in which bending forces are deliberately introduced at the free boundary

of the glue layer so as to tend to split the glue apart progressively.

Fig. 120 shows a standard French test specimen for wood glues³⁴. This specimen is held in special claws which engage in the semi-circular grooves

An ingenious cleavage test for testing the adhesion of surface coatings

has been suggested by ROSSMANN, WEISE and SCHUBBE³⁵. A 0.8 mm diameter hole is punched at the centre of a circular metal disc and this hole is covered with a small piece of metal foil. The surface coating is then applied over the metal foil and the disc; after drying the disc is fixed 1 to

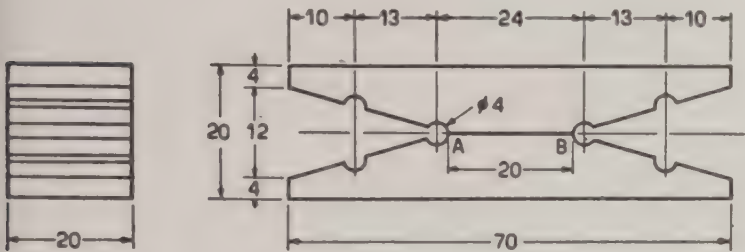


Fig. 190. French cleavage test for wood joints.

The adhesion of electrodeposits* is frequently measured by a cleavage test due to OLLARD³⁶. This test was modified by HOTHERSALL and

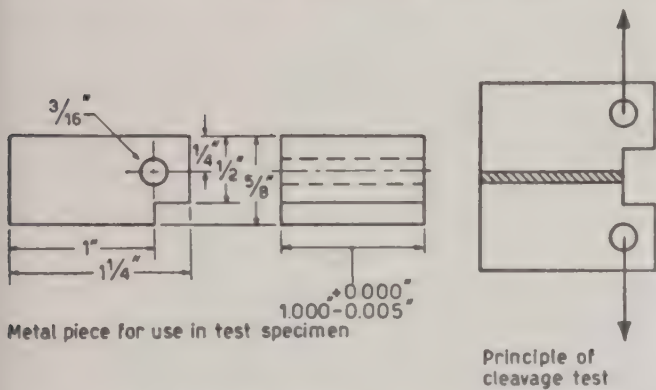


Fig. 191. A.S.T.M. cleavage test for metal to metal joints. Note. The 1 inch square surface to be glued shall be ground flat and parallel with the opposite surface (A.S.T.M. D 903-46).

test (D1062-49T) for metal-to-metal adhesives as outlined in Fig. 191.

(e) Chisel Tests

A variant of the cleavage test consists in forcing a wedge or chisel between the adherends in the plane of the interface between a surface coating and the panel.

Various instruments using this principle are described in GARDNER'S

* The author is indebted to Miss E. W. PARKER of the Mond Nickel Co. Ltd. for supplying a bibliography of papers on adhesion of electrodeposits.

Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours ⁴⁰. Two recent devices of this type are due to GREEN and LAMATTINA ⁴¹ illustrated diagrammatically in Fig. 192, and KOOLE ⁴² of which the principle is shown in Fig. 193.

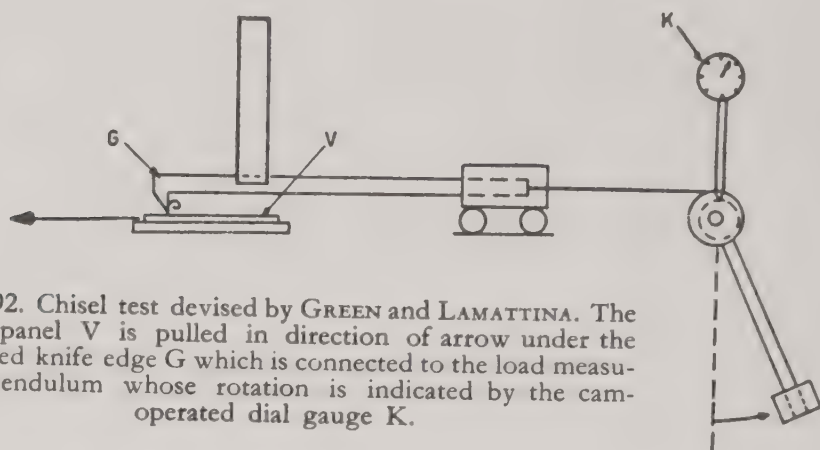


Fig. 192. Chisel test devised by GREEN and LAMATTINA. The metal panel V is pulled in direction of arrow under the weighted knife edge G which is connected to the load measuring pendulum whose rotation is indicated by the cam-operated dial gauge K.

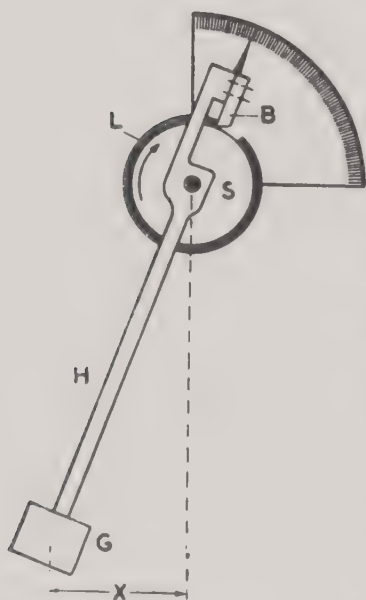


Fig. 193. KOOLE's chisel test. The paint film is applied to the periphery of the steel disc. Arrangement for the measurement of the adhesive force S Steel disc, accurately ground to circular shape; L Lacquer film; H Lever carrying the hard steel chisel B; G Counter weight.

As in peeling tests the force required to detach a film increases with the film thickness.

The interlaminar strength of plastic laminated sheet has been measured by forcing a steel ball into the edge of a test piece and noting the load at which interlaminar rupture takes place; a critical examination of this and similar tests has been made by BARWELL and PEPPER¹⁰¹.

(f) Peeling Tests

Peeling or stripping tests can be made where one or both the adherends are thin, and are of value as representative of conditions to which such a joint may be subjected in practice. The stress distribution in such a test is complex and the force required to initiate and to maintain stripping is considerably influenced among other factors by the dimensions of the specimen and the mechanical properties of the adherends as

well as of the adhesive. A rational analysis of the peeling test has yet to be made.

JACQUET⁴³ has described a peeling test for electrodeposits, and work done at the Bureau of Standards in U.S.A. indicates that the peeling force required to detach a plated strip of thickness from a thick base is proportional to $t^{3/4}$.⁴⁴

A test used by E.M.P.A., although superficially a bending test, is best classified as a peeling test. As shown in Fig. 194 a central load is applied to a bar to which a stiff beam is cemented to the central portion on the lower side.

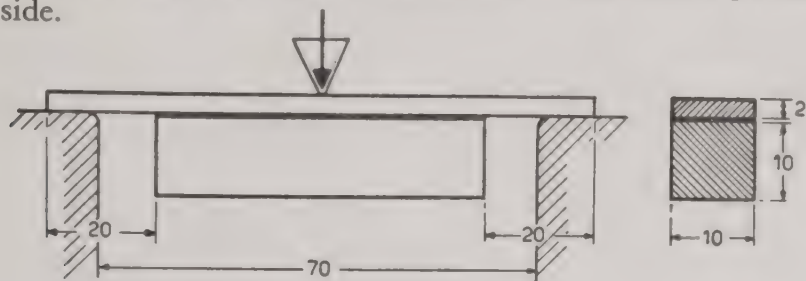


Fig. 194. Peeling produced by bending.

For investigating the peeling strength of joints between 22 s.w.g. light alloys Aero Research Limited use the test shown in Fig. 195⁴⁵. Two metal strips 20

s.w.g. (thickness 0.036 inch or 0.9 mm) 1 inch wide and 7 inches long, made of D.T.D. 390 (Dural with 0.1% proof stress 33,000 p.s.i. and ultimate tensile stress 55,000 p.s.i.) are glued together over their middle $5\frac{1}{2}$ inches and then rolled to a radius of 3 inches. The inner strip is then fixed on a freely

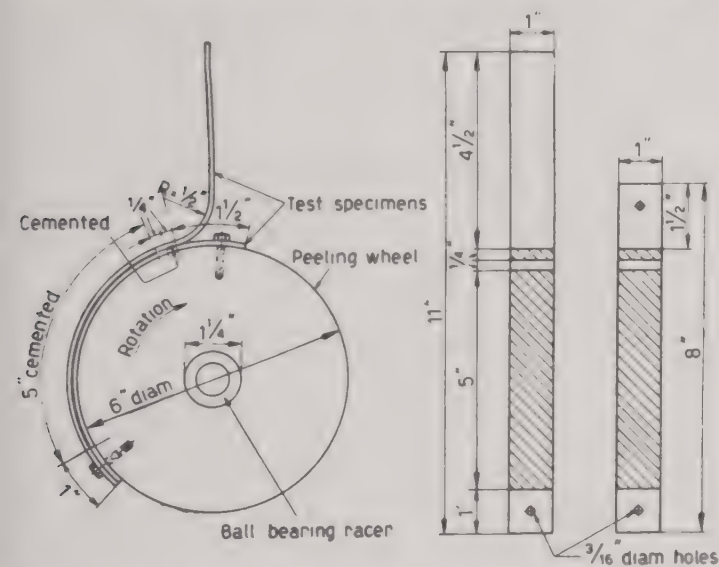


Fig. 195. A.R.L. peeling test. Shaded area shows position of adhesive. Specimens are bonded together in a press, and then rolled to 6 in. dia. and screwed to peeling wheel.

rotating drum of 6 inches diameter, while the outer is pulled radially by one of its ends (Fig. 196). Peeling near the glued end the strip is stressed by bending

beyond its yield point and curves to a radius R much smaller than the radius of the drum. The peeling force P is plotted against the unrolling of the strip (Fig. 197) and is found to vary considerably from point and point.

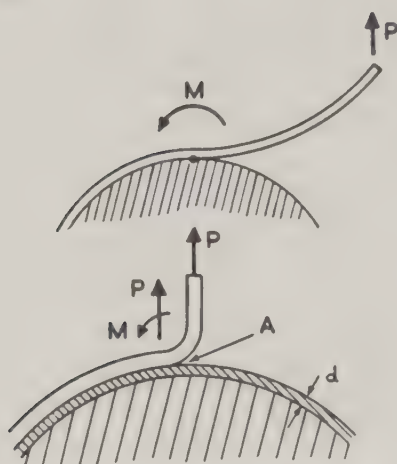


Fig. 196. Bending moment M and applied load P in A.R.L. peeling test.

when the moment is greatly reduced and a considerably higher force P is needed to tear off the strip. Even when the bending of the strip is in the yield region a small change of adhesive strength or strip thickness will be found to result in a very much larger variation of the peeling force. Thus for example a doubling of the peeling force may be caused by an increase by only $\frac{1}{7}$ th of the peeling strength, hence the marked irregularities

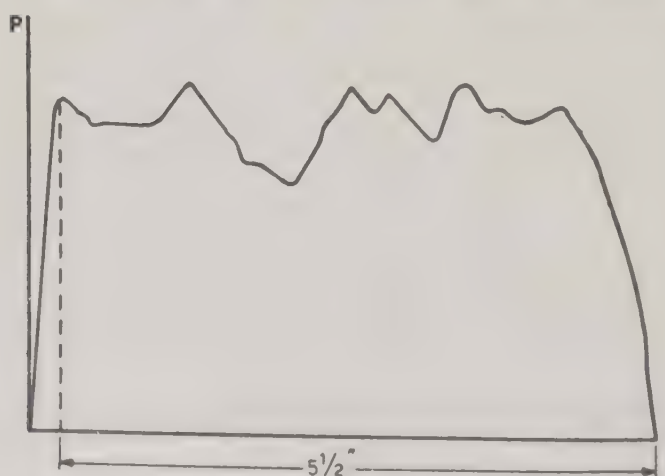


Fig. 197. Autographic curve of load against length peeled obtained in A.R.L. peeling test.

References p. 491

For this reason the highest force as well as the area of the diagram expressed in square centimetres are both taken as indications of the peeling strength as the latter corresponds to an average value of the peeling force. The peeling may start before the strip bends upright and this is an indication that the stiffness of the strip is too high compared with the strength of the adhesive. Then a small force P (Fig. 196) produces a strong bending moment at the point where the peeling starts. A slight increase of adhesive strength or a decrease of strip stiffness (*e.g.* thickness) may make the strip yield and bend as in Fig. 196.

of the peeling diagrams which do not correspond to proportional variations of adhesive strength. For these reasons the peeling test is a very sensitive method for the determination of small changes of strength.

A number of other empirical tests have been devised for measuring the adhesion of gummed tape, and of paint films ⁴⁰.

COURTNEY and WAKEFIELD ⁴⁶ describe an autographic stripping test for surface coatings.

A peeling test, used by SCHREIBER and STAFFORD ⁴⁷ for measuring the

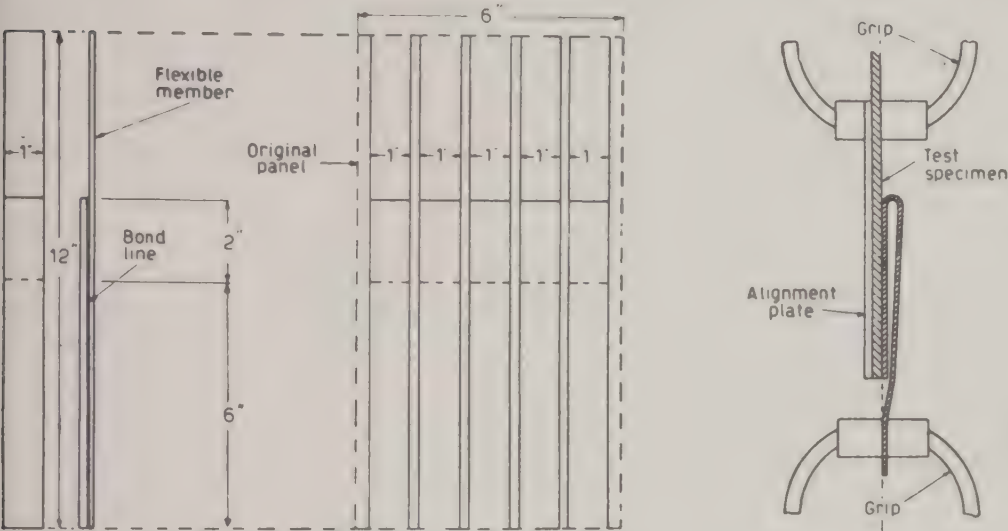


Fig. 198. A.S.T.M. test specimen and method of testing peeling of rubber cements.

extent to which a starched fabric sticks to a heated smoothing iron, consists in using a Jolly spring balance to measure the force required to peel off a piece of fabric from the shoe of a rotary ironing machine.

The sealing quality of paraffin wax has been assessed ¹⁰³ by pressing two pieces of waxed paper together between hot glass plates and then peeling them apart at a fixed rate. ANDERSON ¹⁰⁴ has described a peeling test for two ply rubberized fabric and shown that there is a linear relation between the peeling force and the logarithm of the peeling velocity from 0.05 to 10⁵ mm/minute.

A.S.T.M. Standard (D903-49) for detemining the peeling strength of rubber cements specifies test specimens and test shown in Fig. 198. (cf. Chapter 7).

CHADWICK ⁴⁸ devised the test (cf. Chapter 8) shown in Fig. 199 for measuring the resistance of a soldered joint to tearing. The load during tearing varies in the way shown in Fig. 200. The steady load, following

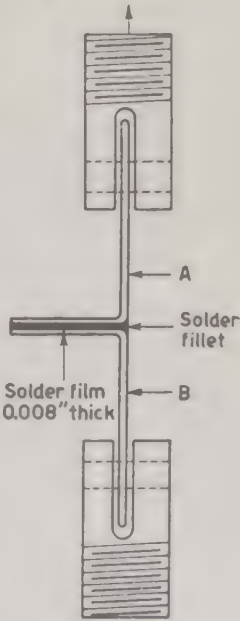


Fig. 199. The CHADWICK peeling test of soldered joints

breaking of the fillet, depends upon the direction of rolling of the sheet as shown in Fig. 201 ⁴⁹.

In all such tests the characteristics of the testing machine have an influence on the results obtained ⁵⁰. Thus if the testing machine is hydraulically operated the peeling load will tend to fall off rapidly if the resistance to splitting falls off momentarily, whereas in a dead weight testing machine there will be no such relief effect. Nevertheless such a peeling test is a useful control of factory bonding and it is a more sensitive test than that of pulling lap joints apart.

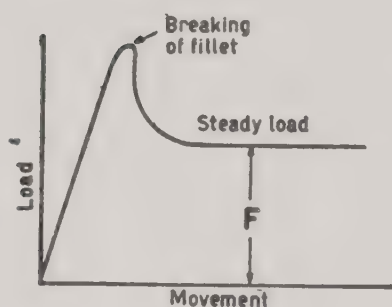


Fig. 200. Autographic record obtained in CHADWICK test.

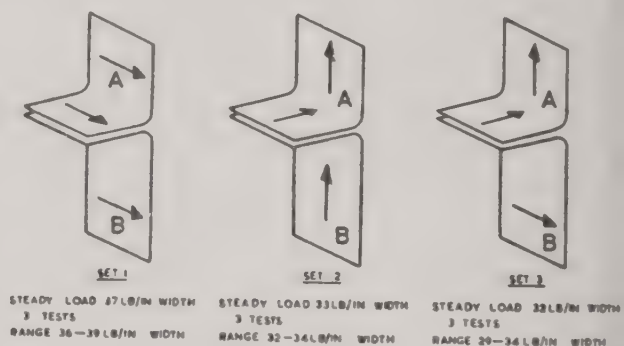


Fig. 201. Influence of direction of rolling of strip on CHADWICK test results. In all 9 cases the solder stripped off the plate A, i.e. the plate in which the direction of rolling was the same as the direction of pulling.

(g) Impact and Fatigue Tests

(i) Impact tests

Impact tests have been made on glued joints and have a practical significance though their interpretation is difficult. A.S.T.M. Tentative Standard D950-47T calls for specimens of the type shown in Fig. 202 for both wood and metal. SILVER ⁵¹ has obtained consistent results with flexible adhesives using this test, provided that the thickness of the adhesive is maintained constant.

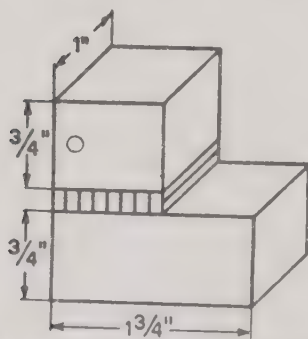


Fig. 202. A.S.T.M. impact test specimen for wood to metal joints.

FALK ⁵² has described an impact test in which a weight falls from a known height on to a tension test specimen. This apparatus can also be used for repeated impact tests. In all impact tests some part of the energy is absorbed in the adherends and in the testing machine ⁵³, and the maximum stress in the adhesive will be greatly influenced by its

flexibility or "resilience" in relation to that of the adherends.

DAVIS⁹⁷ has described a ballistic method for the determination of interply adhesion. SCHMITT⁹⁸ has used a ballistic method for the determination of fresh rubber stocks calendered on fabrics. BUIST, LINDSEY, NAUNTON, STAFFORD and WILLIAMS¹⁰⁷ have described an impact test for rubber-to-metal joints.

(ii) *Fatigue tests*

Fatigue tests can be made on glued joints by repeated application of a given load or given deformation by almost any of the methods used in static tests. In testing wood KOLLMAN found that if the deformation is fixed the machine will frequently continue to run indefinitely after the appearance of splits or cracks in the wood; organic materials differ in this respect in their behaviour to repeated deformation from metals⁵⁴, and it would seem to be preferable to use testing machines where a definite load is applied

by say an out-of-balance rotating weight than one in which a definite deformation is produced by say an eccentric or crank.

Repeated peeling tests have been made by the U.S. Forest Products Laboratory⁵⁶ on both wood-to-metal and wood-to-wood joints, using a KROUSE fatigue testing machine. This method of testing imposes a definite deformation and not a definite stress. It was found better not to use a fully reversed cycle but one in which the stress on the glue varies between zero and a tensile value. Significant differences in the behaviour of different glues have been obtained by this test, particularly with thick glue lines.

DIETZ and GRINSFELDER⁵⁶ have used a similar type of machine to deflect plywood and laminated wood specimens made

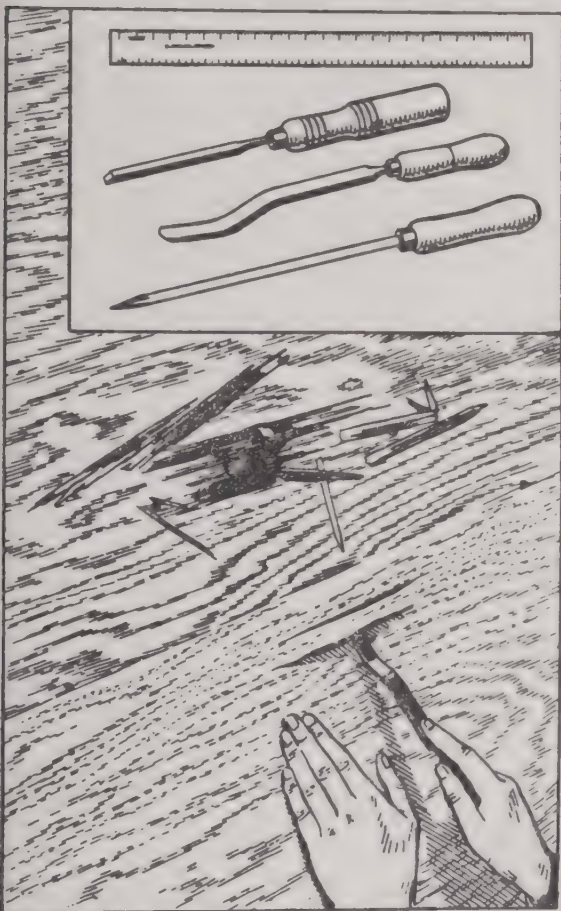


Fig. 203. Subjective chisel test of plywood adhesion.

with phenol-formaldehyde and urea-formaldehyde glues. Fatigue tests under repeated three point loading, as shown in Fig. 187, have been made by the E.M.P.A. on glued wood beams⁵⁷.

The Northern Aluminium Co. Ltd. have made tests of simple lap joints in "Alclad" strips under alternating load applied axially. Similar tests have also been reported in U.S.A.⁵⁸, Switzerland⁵⁹ and Holland¹⁰⁶.

(h) *Other destructive tests*

(i) *Knife test for plywood*

A simple knife or chisel test is often applied to plywood and is specified in B.S. 1455: 1948. It is a subjective test but because of its simplicity has a practical value. Fig. 203 shows the type of tool and manner of use.

(ii) *Piercing test*

A plywood test used at Bruynzeel Fineerfabriek N.V., Zaandam (Netherlands), is a combination of bending and shear load at right angles to the plane of the glue films. A piece of plywood 100 mm \times 100 mm \times 6 mm thick is laid on a steel ring of 90 mm inside diameter and 110 mm outside diameter by 20 mm deep. This ring in turn rests on a supporting frame which automatically centres it in the testing machine (arranged for compressive loading) and raises it to allow clear space for the ruptured test specimen. The plywood is subjected to a central localised compressive load from a solid steel cylinder of 30 mm diameter.

Like the tension shear test the rupture load in a well glued specimen will be characteristic of the wood rather than of the glue. Nevertheless the test may be a useful one and it avoids the need for the rather tricky cutting required in specimens of the type shown in Fig. 175.

(j) *Non Destructive Tests*

Ultrasonic examination of glued joints has been attempted in England but experiments indicate that while the method readily shows up patches of complete lack of adhesion characterised by an air film between adherends, it is not able to differentiate between areas of good and poor adhesion. In the direct transmission method of ultrasonic flaw detection the specimen under test is placed between a source of sound and the detector; this method is more suitable for glued joints than the reflection method.

A useful method of examining plywood up to 3 mm in thickness would seem to be by light transmission using two or three filament lamps, each of 1,000 watts, in a reflector supplied with cooling air by forced ventilation⁶⁰.

(k) *Tests of Tacky Adhesives*

Although, as STEFAN showed ⁶¹, Newtonian liquids will give rise to tacky adhesion, in practice tacky adhesives have complex rheological characteristics. A number of "tackiness meters" have been devised, of which the most recent is that due to LAMBERT and McDONALD ⁶².

Peeling tests are also used for evaluating tacky adhesives, in particular of self-adhesive tapes. GEER and WESCOTT ⁶³ have described a device for testing adhesive tape. A.S.T.M. specification D69-48T describes a simple tackiness test by peeling friction tape off a horizontal surface; specification D1000-48T also describes a peeling test.

A number of Russian workers have described various stripping or peeling test for tacky adhesives ^{64, 65}.

All these tests are of a distinctly empirical character though it is possible to apply to instruments of the type used by GREEN ⁶⁶ and of LAMBERT and McDONALD, an analysis similar to that devised by SCOTT and others for the parallel plate plastimeter ⁶⁷ substituting tensile for compressive loads. Thus for an adhesive with a yield point f of thickness D and volume V between two disc-shaped adherends there will be a limiting force F , below which no separation of the discs can take place, given by:

$$F = 2f V^{1/2} / 3\pi^{1/2} D^{1/2}$$

For a discussion of tackiness in elastomers and of an apparatus for its measurement, see the Chapter by BUSSE, LAMBERT and VEDERY in *High Polymer Physics* ⁶⁸, also Chapter 7.

BLOM ⁶⁹ has described a recording tackiness meter for paints made by E. SCHILDKNECHT of Zürich. A tracing on a drum revolved by a clock shows when the tackiness, as measured by adhesion of a leather surfaced plunger, disappears.

The action of a testing device developed and used by Herts. Pharmaceuticals Limited, Welwyn Garden City, England, for routine tests on pressure sensitive tapes is illustrated in principle in Fig. 204.

A "Tackmeter" for rubber testing has recently been described by BEAVEN, CROFT-WHITE, GARNER and ROONEY ¹⁰⁵.

§ 3. DURABILITY AND AGEING TESTS

Durability tests are made by exposure of representative joints to the particular influence (weather, immersion in solvents, heat and so on) about whose effect information is required. In ageing tests the behaviour of joints

stored under normal conditions (as for example at normal temperature and humidity) is investigated over a period of time which may be months or years; ageing tests are often conducted simultaneously with durability tests to act as controls for them.

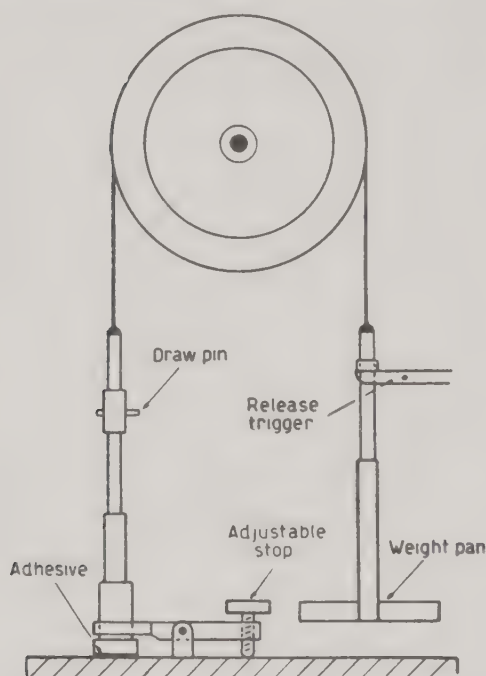


Fig. 204. Test devised by Herts. Pharmaceuticals Limited for pressure sensitive adhesives.

*Adhesives-Series II*⁷², and on ageing tests extending over a period of five years on glued joint⁷³. Tests are also in progress on the weathering of laminated beams. *Durability of Assembly Glues Series B*⁷⁴.

It is difficult to summarise the results adequately and as the investigation is still in progress the latest reports should be consulted.

(b) Other Work on Durability and Ageing

TRUAX and SELBO of the U.S. Forest Products Laboratory have published results of durability tests on laminated beams⁷⁵ subjected to long term exposures and accelerated tests. The accelerated tests consist in subjecting sections of laminated beams 6" by 6" by 3" long to cycles of wetting and drying using an autoclave under vacuum and pressure to facilitate the soaking, and a room at 30% relative humidity and 70° C for drying. Fig. 205 shows the agreement between the two tests.

HOPKINS⁹⁹ has reported on exposive tests on synthetic adhesives and SELBO¹⁰⁰ on the durability of glues for dwellings.

(a) Tests at F.P.R.L., Princes Risborough, England, on Wood Glues

A ten year programme of durability and ageing tests on glued wood joints was begun in 1944 at the Forest Products Research Laboratory, Princes Risborough, England, after initial plywood weathering tests that were started in 1941 and reported by KNIGHT and DOMAN in 1944⁷⁰.

Up to the date of writing Progress Reports have been issued on the results of panel weathering tests on assembly glues, *The Durability of Assembly Glues Series A*⁷¹; on plywood glues, *Weathering Tests on Plywood*

BLOMQUIST¹⁰² has made exposure tests over a two to three year period of joints made with PF and RF adhesives of varying alkalinity.

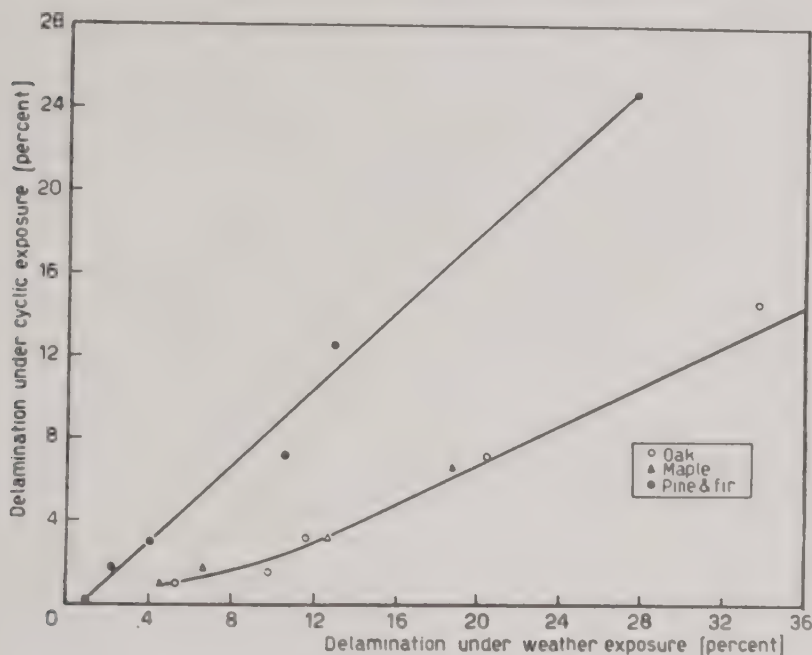


Fig. 205. Comparisons of laboratory and exposure delamination tests. Comparisons of laboratory and exposure delamination tests. Comparison of delamination values obtained with vacuum-pressure soaking-drying cycle and exposure to weather.

BEAULIEU⁷⁶ has reported on the weathering of moulded plywood aircraft components. With the exception of the close contact U.F. resin good durability was found after five and a half years.

WANGAARD⁷⁷ has summarised information on the durability of glues.

BARLOW of the Aluminium Laboratories Research Division, Banbury, England, has investigated the effect on the shear strength of "Redux" joints⁷⁸ in 16 s.w.g. Alclad sheet (D.T.D. 546) and uncoated sheet (D.T.D. 646) of cyclic exposure to a dry atmosphere at 90° C and to 100% relative humidity at 70° C. The shear strength shows a slight drop after twenty cycles of exposure. Ageing tests over two years on specimens in a laboratory have shown no deterioration in joint strength.

A great deal of unpublished work has also been done in England and in U.S.A. on the effect of immersion in solvents, etc., on metal-to-metal joints and for these the manufacturers of the adhesives concerned should be consulted.

LIESE ⁷⁹ describes tests at 40° C and 90–100% relative humidity in the tropical plant room at Eberswalde on plywood made with casein, P.F. film glue and cold setting close contact U.F.; as has been confirmed by later workers it was found that fungicides are not effective in preventing deterioration of casein.

§ 4. SOME OTHER PHYSICAL TESTS

In order to maintain uniformity in the properties of an adhesive a number of physical properties such as viscosity, jelly strength (animal glues), gelation time (synthetic glues), solids content and so on are measured as a matter of routine. For a summary of such tests on vegetable adhesives see B.S. 844 (1951).

(a) *Viscosity*

The viscosity of animal glues in solution is a measure of the degree of polymerisation and therefore of the quality of the protein. In U.S.A. the conditions are laid down in "Federal Specification for Glue No. CG.451 (1931)."

Viscosity tests are widely used for all glues because of the importance to the user of having a material of constant viscosity to facilitate the proper functioning of glue spreaders and similar devices. The viscosity of glues is not usually less than one poise at room temperature and this, together with the tendency of many adhesives to flocculate on addition of solvent, necessitates an instrument that is easily cleaned. It should be a closed instrument to avoid loss of solvents and should work with both opaque and clear liquids. The measurement of viscosity has been thoroughly discussed in such books as BARR's *A Monograph of Viscometry* ⁸⁰ and PHILIPPOFF's *Viskosität der Kolloide* ⁸¹, to which reference should be made. Brief particulars of some of the instruments used for adhesives are given below.

(1) The falling ball viscometer is recommended by the British Plastics Federation in *Proposed Standard Methods for the Determination of the Viscosity of Synthetic Resins* ⁸². This type of viscometer is simple, easy to clean, and in principle is an absolute instrument. Unfortunately it is unsuitable for opaque liquids, though electronic apparatus has been devised to overcome this difficulty ⁸³, and the wall corrections are appreciable unless inconveniently wide tubes are used. Moreover the density of the adhesive must be known. A modification of the falling ball principle is described in A.S.T.M. D.553–42 for rubber cements.

(2) U-tube viscometers ⁸⁴ are accurate and simple in principle but they

are rather inconvenient in routine use as they are not easy to clean and are fragile; they determine, of course, kinematic and not absolute viscosity. U-tube viscometers are recommended for adhesives up to 1550 centipoises in British Plastics Federation Publication No. 21.

(3) The STORMER viscometer has been used to follow the thickening of synthetic adhesives after addition of catalysts by HIGGINS and PLOMLEY⁸⁵. The instrument can be calibrated to measure viscosity in poises⁸⁶.

(4) Rolling ball viscometers such as the HOEPPLER instrument⁸⁷ are suitable and have been used in Germany for measuring the viscosity of adhesives⁸⁸.

(5) GARDNER HOLDT air bubble tubes are a convenient method for rough determinations of kinematic viscosity.

(6) A modified BINGHAM-MURRAY viscometer has been found convenient in the control laboratory of Aero Research Limited. It gives the viscosity in poises without a density determination and is easy to clean⁸⁹.

(7) Efflux Viscometers. The BLOOM pipette viscometer is the standard instrument in U.S.A. and England for animal glues⁹⁰. A.S.T.M. D.553-42 describes a simple efflux viscometer for rubber cements.

(8) Industrial rotational viscometers such as the Brookfield, Dobbie-McInnes or Ferranti instruments are rapid and direct reading but need large samples and are somewhat expensive.

(b) *Jelly Strength*

The strength of a gel of animal glue has long been recognised as a convenient index of its quality, and the most widely used instrument is the BLOOM gelometer⁹⁰ in which a cylinder is pressed into the gel at a rate of loading of 40 grams a second. The load required to produce a 4 mm depression is determined⁹¹.

Other instruments for finding the jelly strength are described in *Chemie und Technologie der Leim- und Gelatine-Fabrikation* by GERNGROSS and GOEBEL⁹².

(c) *Gelation Time*

The determination of the "Pot Life" or "Usable Life" or "Gelation Time" of synthetic adhesives is important both as a control test in manufacture and as a quantity of fundamental importance to the user. It is usually defined as the time, measured from the moment of addition of the catalyst, for the adhesive to reach a condition of high elasticity. The point of transition from the liquid to the gel state is usually quite sharp and easily found by stirring the mixed glue with a rod; it is important that the mixed glue should be maintained at a constant temperature in a suitable water bath.

The setting of phenolic glues at room temperature is accompanied by considerable evolution of heat. For this reason the gelation time of such glues determined under isothermal conditions will be greater than that observed by a customer under works conditions.

A device for measuring gelation time has been described by DE BRUYNE and has given good results ⁹⁶.

(d) *Solids Content*

The determination of the solids content by heating a specimen to remove solvents is an unreliable test because (1) of the tenacity with which solvents are held, and (2) the tendency of thermosetting resins to condense and split off volatiles when heated. Nevertheless such a test has some value for comparative purposes if done under strictly controlled conditions. The British Plastics Federation has tentatively suggested conditions for finding the loss of weight in heating ⁹².

A.S.T.M. D.553-42 specifies a procedure for finding the solids content of rubber adhesives containing organic solvents, and D.640-44 for latex.

Determination of the apparent moisture content of animal glues is described in U.S. Federal Specification CG.451 (1931.)

For any given adhesive the determination of refractive index is often a useful rapid method of finding total solids content.

(e) *Flash Point*

The flash point tests are those developed for petroleum products ⁹³.

(f) *Stability*

Synthetic resins are usually unstable materials with a finite "shelf life". It is usual therefore for the manufacturer to carry out accelerated stability tests by heating the adhesive (without catalyst) at a temperature much above room temperature to assess the probable life of the adhesive when stored at room temperature.

(g) *Flow Characteristics*

The rheological behaviour of a glue during setting is one of the main factors determining the effectiveness of the glue in the hands of the user. It is unfortunate therefore that at present no instrument is available for

assessing the flow properties of an adhesive after the addition of the catalyst or under the influence of rising temperature (at the rapid rate encountered for example in a plywood press). A device of such a type is commonly used for the production control of moulding materials⁹⁴, and instruments are also available for observing the behaviour of starch pastes under rising and falling temperature⁹⁵, but no suitable device is at present available for the type of thermosetting adhesive used for example in the manufacture of plywood.

(h) *Heat of Reaction*

Some synthetic adhesives, in particular cold setting phenolic resins, evolve a significant amount of heat after addition of the catalyst. Measurement of the heat of the reaction is used as a control test and the British Plastics Federation has suggested a specification for carrying out the test.

(i) *Resistance to Chemicals*

A.S.T.M. Tentative Standard D. 896-50T specifies tests of resistance of adhesives to a number of organic and inorganic liquids.

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AUTHOR INDEX

- Abel, J. G. 346, 348
 Abraham, H. 250
 Adams, O. 127
 Adler, E. 248
 Akker, J. A. van den 347
 Aleck, B. J. 120
 Alexander, J. 385
 Alexander, W. 345
 Alfrey, Turner 44
 Alfrey Jr., T. 277
 Ambelong, J. C. 423
 Amero, J. J. 384
 Amerongen, G. J. van 423
 Anderegg, F. O. 77
 Anderson, S. L. 481
 Annis, H. M. 491
 Anderson, A. P. 277
 Arisz, L. 88
 Arnold, K. A. 347
 Askalonov, A. A. 385
 Askew, F. A. 59
 Austin, L. W. 383
 Ayers, L. R. 347
 Baas, P. W. 277
 Bacon, L. R. 285
 Bacon, R. F. 362
 Baker, C. L. 287, 313, 349, 385
 Baker, W. A. 458, 459
 Barber, C. L. 462
 Barkhutt, R. A. 219
 Barlow, D. A. 487
 Barr, G. 488
 Barron, H. 422
 Bartenev, S. 424
 Barwell, F. T. 478
 Bass, S. L. 213
 Bassist, E. 348
 Bauschinger, 471
 Beach, R. L. 306
 Beaulieu, L. A. 487
 Beaven, E. W. J. 485
 Bechtel, W. G. 494
 Beck, J. 58, 68
 Beinlich, A. W. 359
 Bekkedahl, N. 423
 Bellinson, H. R. 77
 Benner, R. C. 346
 Bennett, H. 357, 383
 Benson, D. G. 301
 Berg, 89
 Berge, J. van den 277
 Besele, I. 349
 Bettelheim, L. 247
 Bettendorf, H. J. 304, 344
 Beverdam, H. J. 86, 87
 Bikerman, J. J. 64, 65, 74, 76, 143, 293
 423
 Bickley, W. G. 143
 Biddle, A. 291
 Billitzer, J. 281
 Bingham, E. C. 285
 Biondi, F. J. 494
 Bircumshaw, L. L. 439
 Bittner, J. 464, 492
 Blaikie, K. G. 249
 Blake, J. T. 422
 Bloc, A. 422
 Blokker, P. C. 277
 Blom, A. V. 485
 Blomquist, R. F. 487
 Blow, C. M. 33, 424
 Blum, W. 346
 Bock, E. 492
 Boeder, P. 88
 Boer, J. H. de 8
 Bogue, R. H. 383
 Bohlander, H. 348
 Bohmer, W. 383
 Bollenrath, F. 143
 Boller, E. R. 282, 287, 293, 312, 313, 314,
 319, 320, 321, 323

- Bolton, H. L. 383
 Boroff, E. M. 424
 Borro, E. F. 494
 Boughton, W. A. 348
 Bouton, G. M. 444
 Bowden, F. P. 76
 Bowen, A. H. 349
 Boxer, F. N. 349
 Boyd, G. E. 8
 Boyer-Kavenoki, F. 32
 Brashear, 434
 Breitung, M. 346
 Bretano, W. 200
 Brien, 89
 Brimhall, B. 200
 Britt, K. W. 298, 348
 Brouse, D. 284, 302
 Brown, G. G. 493
 Brown, K. C. 77
 Browne, F. L. 47, 48, 284, 302
 Bruce, D. S. 384
 Brunt, C. van 346
 Bruyne, N. A. de 30, 73, 74, 81, 91, 94, 97
 98, 111, 136, 222, 463, 490
 Buchan, S. 418
 Bucko, G. 424
 Budgett, H. M. 74, 113
 Buist, J. M. 423, 494
 Bulkley, R. 76
 Burger, E. E. 125, 297
 Burgess, C. F. 491
 Burgess, L. L. 280
 Burk, R. E. 248
 Burnett, R. S. 341, 348
 Busse, W. F. 62, 70, 493
 Byall, R. D. 349

 Cadwell, S. M. 423
 Caesar, G. V. 200
 Cairns, W. J. 114
 Camps-Campins, F. 292
 Cann, J. Y. 344
 Carleton, P. W. 291
 Carlson, T. A. 306
 Carswell, T. S. 219
 Carter 244, 298, 303, 327, 330, 334, 339, 384
 Casimir, H. B. G. 32
 Cedwall, J. 247

 Chadwick, R. 446, 481
 Chakrabarty, S. K. 281
 Chalmers, B. 435, 436
 Chambers, R. R. 423
 Chapman, F. 201
 Cheek, D. L. 344
 Clapp, W. F. 346
 Clark, J. d'A. 347
 Clark, W. I. 424
 Clash, 89
 Cleveland, T. K. 342
 Cohen, R. C. 345
 Coker, E. G. 134
 Collier, S. 348, 384
 Collins, W. G. 348
 Collinson, H. A. 249
 Colt, E. W. 183
 Cone, C. N. 349
 Connor, 89
 Conros, C. M. 491
 Cooper, B. 132
 Corbin, W. S. 348
 Cornie, P. Y. 424
 Cornwell, E. D. 47, 50, 147
 Cotton, F. H. 423
 Courtney, R. P. 481
 Croft-White, P. G. 485
 Crow, T.B. 75, 143, 462, 491
 Crowe, G. A. 247
 Crozier, R. N. 249
 Curll, V. A. 383
 Cushing, M. L. 200

 Daniels, E. J. 447
 Darge, E. 384
 Davidson, G. 348
 Davis, C. C. 422
 Davis, F. V. 483
 Davis, H. D. 494
 Davis, H. S. 362
 Davis, R. J. 237
 Dawson, D. N. 493
 Dean, W. T. 348
 Dear, P. S. 297
 De Boer, J. H. 8
 De Bruyne, N. A. 30, 73, 74, 81, 91, 94
 97, 98, 136, 222, 463, 490
 Debye, P. 20

- De Lalande, A. 422
 Delmonte, J. 223, 242, 245, 423
 De Lollis, N. J. 249
 Deluzenne, C. 346, 348
 Demongeot, A. 423
 Denning, P. S. 383
 Denson, C. E. 249
 Dent, B. M. 90
 Derjagin, B. W. 69, 493
 Derksen, J. C. 40
 Desch, C. H. 383
 De Vries, J. 90
 De Wolff, P. de 383
 Dickinson, John 329
 Dietz, A. G. H. 117, 483
 Dietz, K. 384
 Dike, T. W. 348
 Dobry, Mme A. 32
 Doman, L. S. 486
 Doolittle, A. K. 30, 89
 Doty, P. M. 25
 Douglas, W. D. 471
 Dow, J. 64
 Driscoll, J. 384
 Dsjadelj, 424
 Dubrisay, R. 206
 Duecker, W. W. 362
 Dulac, R. 348

 Earle, I. G. 439
 Earle, R. D. 424
 Edas, S. R. H. 348
 Edwards, 447
 Egner, K. 142
 Einhorn, 207
 Ericson, R. 348
 Esch, W. 424
 Esselen, G. I. 246
 Euler, H. von 248

 Fabritzief, B. 424
 Falk, A. H. 482
 Farber, H. 346
 Farberov, M. I. 424
 Farrow, C. A. 48
 Ferri, C. 40
 Filon, L. N. G. 126
 Finlayson, D. 424

 Fisch, W. 247
 Fisher, C. H. 238
 Fisher, H. L. 424
 Fisher, J. C. 143
 Fisher, R. B. 424
 Flint, C. F. 423, 424
 Flory, P. J. 32
 Ford, F. F. 424
 Forest Products, Research Laboratory,
 U.S. 249
 Forrester, P. G. 451
 Fowler, G. B. 348
 Fraass, A. 268
 Frank, K. 384
 Franke, F. W. 346
 Franke, W. F. 340
 Franklin, G. L. 346
 Frederick, Walter 178
 Frey, K. 215
 Fritzius, C. P. 33, 470
 Frocht, M. 475
 Fromandi, G. 421
 Fuchs, J. N. von 278
 Funk, C. S. 494

 Gander, R. J. 423
 Ganguly, P. B. 280, 281
 Gams, A. 209, 210
 Gardner, E. P. S. 94
 Gardner, E. R. 424
 Gardner, H. A. 477
 Gardner, H. F. 282
 Garner, E. 346
 Garner, P. J. 485
 Garriot, F. E. 384
 Garrison, A. D. 385
 Gassot, J. 424
 Gearheart 89
 Geddes, J. A. 493, 494
 Gee, G. 8, 18
 Geer, W. C. 485
 Génin, G. 422
 Gerngross, O. 149, 489
 Gilbert, N. 359
 Gill, F. G. 345
 Gilliam, W. F. 213
 Gilman, H. H. 424
 Gilman, L. 32

- Gilmore, K. E. 344
 Giva, 208
 Goebel, E. 149, 489
 Goland, M. 101, 102, 103, 120, 132, 142
 Goldschmidt, C. 207
 Gonser, B. W. 458
 Gorina, A. I. 424
 Gottschalk, G. W. 423
 Graf, O. 142
 Granger, F. S. 219
 Granholm, H. 104
 Grasselt, H. M. 348
 Greaves-Walker, A. F. 368
 Green, H. 58, 288, 485
 Green, R. E. 347, 477
 Greenfield, L. T. 451
 Greenup, H. W. 349
 Grinsfelder, H. 117, 483
 Groh, H. 349
 Grosert, J. E. 493
 Gruenhut, N. S. 200
 Grummitt, O. 248
 Gumprich, C. 345
 Gundlach, H. R. 348
 Guth, E. 32

 Habgood, B. J. 424
 Hackel, W. 345
 Haim, G. 384
 Hakanson, H. 337
 Hale, H. M. 348
 Hall, F. P. 384
 Hall, H. Warburton 491
 Haller, W. 88
 Hamaker, 42
 Hamley, D. H. 48
 Hammond, G. L. 424
 Hanson, J. E. 494
 Hanus, F. 248
 Harkins, W. D. 8
 Harman, R. W. 280
 Harnden, G. H. 469
 Harris, F. C. 143
 Hartmann, A. 225, 492
 Hays, J. B. 385
 Hazard, F. O. 383
 Hazerl, J. F. 281
 Healy, 66

 Hearmon, R. F. S. 142
 Heath, 458
 Hedges, E. S. 462
 Heindl, R. A. 371
 Hendricks, J. O. 62, 423
 Hendricks, S. B. 297
 Henley, N. W. 383
 Herzmann, D. B. 277
 Hetényi, M. 127
 Heukelom, W. 277
 Hibben, J. H. 281
 Higgins, H. G. 489
 Hildebrand, J. H. 17, 18, 222
 Hirobe, H. 25
 Hoare, W. E. 447, 454
 Höchtlen, A. 247
 Hodgins, T. S. 247
 Hoekstra, J. 33, 88, 470
 Hoeppler, F. 489
 Hollander, H. 181
 Holt, F. 349
 Homer, C.E. 462
 Hook, Thomas D. 178
 Hopkins, D. G. 345
 Hopkins, R. P. 486
 Horig, H. 142
 Hothersall, A. W. 477
 Houwink, R. 3, 8, 42, 88, 89, 90, 218, 311, 423

 Hove, A. E. H. 142
 Hovey, A. G. 247
 Hovgaard, H. 104
 Howard, W. 93
 Hubbard, R. M. 493
 Hubbell, D. S. 355
 Hudson, O. F. 455, 492
 Huggins, M. L. 32
 Hull, A. W. 125, 297
 Hultsch, K. 248
 Humberstone, J. H. 384
 Husemann, E. 200

 Inglis, C. E. 134
 Insley, H. 384

 Jackson, T. 424
 Jacquet, M. P. 479
 James, H. M. 32

- Jarryon, A. 424
Johansson, C. E. 90
Johnson, C. B. 173
Johnson, O. 349
Johnston, G. B. 344
Jonas, B. 90, 143
Jones, 89
Jones, E. 242
Jones, F. A. 424
Jones, F. D. 74
Jones, W. D. 435, 447
Jones, W. L. 343
Jura, G. 8

Kalin, L. 346
Kaplan, A. B. 347
Katz, D. L. 316, 318, 319
Keesom, W. H. 20
Kemner, H. 349
Kemp, A. R. 277
Kent, 89
Kerr, R. W. 200
Kesler, C. C. 494
Kidder, 89
Killeffer, D. H. 383
Kipping, F. S. 213
Kirchner, H. P. 346
Klaassens, K. H. 88
Kleeberg, W. 247
Kline, G. M. 247
Knight, R. A. G. 485
Koehler, R. 209, 210, 211, 247
Kohlrusch, F. 280
Kollmann, F. 483, 491, 492
Konstantinova, W. P. 74, 113, 143
Koole, P. 478
Kraemer, O. 491
Kreyling, L. R. 347
Krishnamurti, D. 344
Kroeber, M. 218
Kronman, S. J. 383
Kuhn, W. 37
Kyrning, S. 248

Laar, J. J. van 17
Labout, J. W. A. 88, 277
Lachman, M. 301
Lacolange 424

Ladwig, A. 351
Lafume, H. 384
Lalande, A. de 422
Lambert, J. M. 62, 70, 485
Lamattina, T. P. 478
Lander, J. G. 282, 287, 312, 319, 320
Lane, L. B. 183
Langmuir, L. 18
Lantz, E. A. 493
Larson, L. L. 349
Lasher, L. 383
Lashev, E. K. 348
Latin, A. 437, 439, 445
Laucks, I. F. 348
Lavell, S. J. 32
Lavery, J. H. 492
Laws, W. D. 384
Lea, F. M. 383
Leadbeater, C. V. 477
Le Bras, J. 422
Lee, W. B. 30, 73, 76, 82, 142, 345, 383, 491
Lee, William M. 184
Leighou, R. B. 383
Leilich, K. 89
Lemmerman, P. C. 291, 346
Lennard-Jones, J. E. 76
Lentze, H. 424
Leonard, F. 32
Lewis, C. A. 183
Lewis, W. R. 427, 462
Liddiard, P. D. 290
Liebig, J. 208
Liese, J. 488
Lindner, G. F. 62, 423
Lindsey, C. H. 483
Littig, G. 349
Little, G. E. 217, 219, 221, 306
Littleton, J. T. 143
Llewellyn, F. T. 348
Loddengaard, P. M. 183
Lollis, N. J. de 249
London, F. 19
Long, O. 304
Louia, P. 424
Lozovskaya, J. 424
Luchtvaart Laboratorium, Nationaal 248
Lynch, C. C. 247
Lyons, W. J. 491

- MacMahon, J. D. 384
 Magat, M. 16, 17
 Malcolmson, J. D. 282, 348
 Mallman, W. L. 383
 Mang, A. 349
 Mann, J. C. 90
 Mark, H. 25, 32
 Martin, S. R. W. 247
 Marvel, C. S. 207, 208, 249, 423
 Maslem, K. R. 242
 Mason, C. F. 383
 Mathias, D. L. 384
 Maupin, A. R. 449
 Maxwell, J. W. 48, 75
 McAllister, D. 384
 McBain, J. W. 30, 47, 73, 76, 82, 142, 283
 291, 298, 302, 383, 491
 McCready, D. W. 306, 316, 317, 318, 319,
 321, 322
 McCulloch, L. 349
 McDonald 181, 485
 McFarlane, J. S. 114
 McKee, R. C. 347
 McKeown, J. 456, 458, 461, 492
 McKinney, P. V. 364
 McLaren, A. D. 30, 237
 McLean, D. A. 298
 McLaurin, W. W. 469
 MacNaughtan, D. J. 462
 Meerkamp van Embden, H. J. 90
 Megson, N. J. L. 218
 Meissner, H. P. 116, 491
 Melton, R. L. 346
 Merrill, E. W. 116, 491
 Merrill, R. A. 423
 Merrill, R. C. 298, 383
 Meyer, H. 424
 Meyer, K. H. 40, 200, 247
 Meyrick, T. J. 424
 Mican, G. S. 384
 Miller, W. L. 348
 Mitchell, W. M. 301
 Moakes, R. C. W. 424
 Möhrle, A. 384
 Molisch, F. 344
 Montandon, R. 77, 143, 491
 Mooney, R. C. L. 249
 Moore, B. 383
 Morehouse, R. 282, 287, 312, 319, 320
 Morey, G. W. 383
 Morgan, G. T. 248
 Morgan, W. R. 383
 Moser, F. 5
 Moses, S. 467
 Moss, C. J. 143
 Muhlenbruch, C. W. 476
 Murphy, 89
 Mylonas, C. 73, 74, 81, 91, 102, 103, 126
 132, 136, 138
 Myrback, K. 200
 Nagai, S. 383
 Naunton, W. J. S. 423, 483
 Nazzaro, R. 343
 Nellensteyn, F. J. 277
 Nelson, L. M. 491
 Newall, R. J. 493
 Nightingale, S. J. 455, 492
 Noble, R. J. 349
 Nocent, M. 385
 Nijboer, L. W. 277
 Nye, F. J. 143
 Okoleluikh, V. I. 385
 Ollard, E. A. 477
 Oosterhof, D. 277
 Ordway, J. M. 344
 Orlov, A. I. 493
 Orowan, E. 114
 Ott, G. H. 248
 Padmos, A. A. 90
 Paffenbarger, G. C. 376, 378, 380, 381, 383
 Page, J. B. 384
 Painter, W. S. 348
 Pakomova, E. 424*
 Parker, E. D. 341
 Parker, E. R. 437
 Partridge, J. H. 121, 127
 Pattilloch, D. K. 348
 Payne, C. R. 349, 362
 Peakes, C. R. 349
 Peek, R. L. 90
 Peirce, F. T. 77
 Pell-Walpole, W. T. 455
 Pendergast, W. L. 371

- Pepper, K. W. 217, 219, 478
 Perry, T. D. 348
 Peskin, W. L. 383
 Petelin, G. I. 424
 Pfeiffer, J. Ph. 252
 Philippoff, W. 488
 Phipps, G. S. 444
 Pitt, N. P. 345
 Pittman, C. U. 277
 Pittman, G. A. 423
 Plaizier, J. A. 423
 Plantema, F. J. 103
 Plomley, K. F. 489
 Poel, C. van der 277
 Pohl, R. W. 143
 Polder, D. 32
 Pole, G. R. 359
 Poletika, N.V. 75, 76
 Poole, J. P. 365, 366
 Poretskaja, A. P. 69, 493
 Poritsky, H. 125
 Powell, G. M. 30
 Powell, R. E. 348
 Powers, P. O. 204
 Poynting, J. H. 89
 Preece, 447
 Privinsky, F. 384
 Proske, G. 424
 Prytherch, J. C. 452
 Puddefoot, L. E. 423, 424
 Purdon, A. O. 350, 351

Quinn, D. L. 305, 306

 Raccin, 208
 Ramsey, G. S. 424
 Randolph, F. T. 348
 Rasmussen, T. J. 384
 Rawson, H. 125
 Reach, M. I. 337
 Redston, G. D. 143
 Reed, R. F. 68, 89
 Reissnurm, E. 101, 102, 103, 117, 120, 132, 142
 Remler, R. F. 313, 314, 346
 Rendle, B. J. 346
 Rennie, N. G. 347
 Reynolds, O. 64
 Rhodes, D. 383

 Ricardo, Sir Harry 464
 Richards, A. P. 346
 Richmond, T. M. 304
 Rideal, E. K. 348
 Rife, P. 346
 Rivlin, R. S. 60, 70
 Robie, N. P. 304
 Robinson, E. B. 424
 Robinson, W. W. 383
 Rochow, E. G. 213
 Röder, H. L. 43
 Roehl, E. S. 477
 Roeser, G. R. 32
 Rogers, S. S. 423
 Rohm, O. 237
 Rojas, F. A. 300
 Roodenburg, N. M. 277
 Rooney, E. 485
 Rooijen, J. M. van 277
 Ros, M. 492
 Rosenbaum, J. L. 348
 Rossem, A. van 86, 87, 423
 Rossmann, E. 477
 Rowland, B. W. 298
 Rucker, N. 249
 Rudeloff 466

 Saal, R. N. J. 88, 90, 250, 277
 Sadtler, S. S. 383
 Salomon, G. 386, 423
 Sams, R. H. 281, 288, 347, 348, 349, 477
 Sanger, R. 248
 Sarason, M. 344
 Sarbach, D. V. 424
 Schaefer, C. F. 384
 Schaefer, W. D. 8
 Schildknecht, E. 485
 Schlitt, W. 424
 Schmidt, E. K. O. 467
 Schmitt, E. 483
 Schoch, T. J. 200
 Schönlau, W. J. K. 386
 Schreiber, W. T. 481
 Schubbe, A. 477
 Schumacher, E. E. 444
 Schupp, O. E. 293, 319, 321
 Schwartzwalder, K. 384
 Schweitzer, W. K. 346

- Scott, A. F. 32
 Scott, H. 123
 Scott, J. R. 57, 66, 90, 111, 493
 Scott, W. J. 127
 Seabright, L. H. 462
 Segesser, J. R. 494
 Seiler, Charles 32
 Selbo, M. L. 486
 Sharp, E. R. 291
 Shattuck, R. 424
 Sheely, M. L. 183
 Sheets, G. H. 347
 Sheperdson, 424
 Shimanko, A. F. 348
 Shute, R. L. 384
 Siefen, J. F. 384
 Siegfried, W. 248
 Silver, J. 32, 482
 Singer, F. 383
 Skinner, E. W. 353
 Sloman, C. M. 423
 Smelt, J. 90
 Smith, E. A. 48
 Smith Jr., G.E.P. 423
 Smith, W. R. 8
 Smoluchowski, R. 437
 Smythe, E. 247
 Snell, F. D. 384
 Snijder, J. W. 88
 Soane, G. E. 493
 Sokolovskii, A.N. 384
 Sontag, L. A. 494
 Souder, W. 376, 378, 380, 381, 383
 Southwell, R. V. 492
 Sovokin, S. M. 493
 Späth, W. 492
 Spear, 345
 Speitman, M. 493
 Spencer, R. W. 298
 Speyer, A. 247
 Stafford, W. L. 481, 483
 Stäger, H. 90, 248, 491
 Stanworth, J. E. 143
 Starkweather, H. W. 424
 Staudinger, H. 200
 Staverman, A. J. 8, 9, 82
 Stefan, J. 63, 64, 485
 Steinberg, R. H. 384
 Stengle, 181
 Stephan, J. 90
 Stericker, W. 280, 288, 298, 342
 Stern, E. 348
 Stewart, J. K. 424
 Stiehler, R. D. 423
 Strain, D. E. 239
 Stranski, I. 8
 Subarov, N. 348
 Sugimoto, S. 218
 Sun, K. H. 297
 Svedberg, T. 280
 Swanger, W. H. 449
 Sward, G. G. 492
 Swindells, J. F. 345
 Swire, W. H. 424
 Symes, E. M. 493
 Tabor, D. 114
 Taylor, N. W. 297
 Taylor, R. L. 277
 Teague, M. C. 349
 Thalmud 56
 Thickens, J. H. 334
 Thinius, K. 31, 222
 Thoman, R. 424
 Thompson, R. H. 304
 Thompson, T. D. 348
 Thomson, G. M. 348
 Thomson, J. J. 89
 Thornley, E. R. 423
 Thring, M. W. 143
 Throckmorton, E. A. 347
 Timoshenko, S. 93
 Tobolsky, A. V. 32
 Toland, W. C. 348
 Traxler, R. N. 277
 Treloar, I. R. G. 32
 Troelsch, H. W. 104
 Truax, T. R. 47, 48, 149, 486
 Turner, P. S. 116, 423
 Turner, W. E. S. 346
 Twiss, D. F. 424
 Tylecote, R. F. 143
 Urbans, S. F. 384
 Ursprung, A. 143

- Vail, J. G. 281, 287, 298, 299, 307, 315
Vana, C. A. 349
Van Amerongen, G. J. 423
Van Brunt, C. 346
Van de Berge, J. 277
Van den Akker, J. A. 347
Van der Poel, C. 277
Van Laar, J. J. 17
Van Rooijen, J. M. 277
Van Rossem, A. 86, 87, 423
Verdery, R. B. 62, 70, 485
Vincent, R. S. 32
Voet, A. 59, 69
Volkersen, O. 97, 101, 133, 142
Von Euler, H. 248
Von Fuchs, J. N. 278
Vries, J. de 90

Wadie, R. H. 436
Wagner, F. C. 424
Wake, W. C. 424
Wakefield, H. F. 481, 491
Waldeck, H. 385
Walter-Levrard, L. 383
Walters, H. W. 300
Walther, C. 256
Wangaard, F. F. 487
Ware, W. C. 279, 291, 300, 340
Watts, J. T. 424
Weaver, 89
Webb, H. W. 384
Weber, L. 384
Wegst, W. F. 333, 345
Wehmer, F. J. 62, 423
Weir, S. E. 249
Weise, K. 477
Wells, S. D. 347
Wennstrom, A. F. 383
Went, J. J. 90

Werner, A. W. 347
Wescott, W. B. 485
Westwater, J. W. 475
Wexler, A. 298
Weygandt, A. S. 349
Weyl, W. A. 32, 281, 298
Wicker, C. R. 494
Widmer, G. 247
Wiegand, W. B. 40
Williams, G. E. 247, 483
Williams, P. L. 424
Wills, John H. 278, 281, 288, 347, 348, 477
Winks, F. 346
Winterkorn, H. F. 384
Wisman, 89
Witt, R. K. 467
Wittrick, W. H. 93
Wojuzki, 424
Wolff, P. de 383
Wood, E. 462
Wood, C. D. 293
Wood, R. G. 247
Wooten, L. A. 298
Wright, K. A. 277
Würstlin 89
Wurtz 247

Yost, F. L. 423

Zable, Helen S. 25
Zavjalov, I. N. 287
Zhukov, 56
Zhuravlev, H. 424
Ziegler, E. 248
Zinke, A. 248
Zschokke, H. 77, 143, 491
Zsigmondy, R. 281
Zueva, L. D. 424

SUBJECT INDEX

- Abrasives, surface-coated 161
- Absorbing layers, topography 7
- Acetate rayon, adsorption and desorption of water 83
- Acid hydrolyzed starches 184, 198
- Acrylic resins 237
- Adherend, porous or absorbent 222
- Adherends, mechanical properties, 110
 - , non-porous or non-absorbent 222
 - and adhesive, differential thermal contraction 116
 - — — , mechanical properties 110
- Adhesion 12
 - , conditions 5
 - , energy of 14
 - in soldered joints 427
 - , mechanical 47
 - of anti-friction alloys to tinned surfaces 450
 - of glass to metal 127
 - of rubber to metals 407
 - of surgery plasters 60
 - , physical testing 463
 - , specific 47
- Adhesive(s), application 46
 - based on rubber solutions 401
 - , cellulose nitrate 246
 - , cold-setting 233
 - , cyclized rubber 415
 - , dextrine 188
 - , end use tests 463
 - , fluid 397
 - for joining glass to steel 400
 - , hot-setting 227
 - , influence of temperature 85
 - , inorganic 278
 - , internal stresses 84
 - , latex-based 398, 399
 - layer(s), flexible 101
 - — , thin 76, 99
 - — , thin inflexible 106
- Adhesive(s), long 63
 - , melanine-formaldehyde 208
 - , organic 147
 - , phenolic resin 203
 - , physical testing 463
 - , plastic flow 79
 - , polyvinyl-acetate 242
 - , pressure sensitive-test 486
 - , production control 463
 - , resorcinol-formaldehyde 205
 - , rubbery 386
 - , setting 71
 - , short 63
 - , silicate 309
 - , sodiumsilicate (constitution; properties) 280
 - , synthetic resin 201
 - , — — (production and sales) 202
 - tape 61, 62, 421
 - test joints, plywood 468
 - , thermoplastic 201, 234, 412
 - , — (application) 245
 - , thermosetting 201
 - , thixotropic 50
 - , urea-formaldehyde 206
 - , vegetable 184
- Adsorption of water by textiles 83
- Aerolite resin 49
- Ageing tests (glued joints) 485, 486
- Alkali conversions of starch 192
- Alloyed coatings 433
- Alloying (solder) and spreading 348
- Alpha amylase 194
- Aluminium, adhesion to silicate 284
 - , treatment of (before soldering) 433
- Aluminium alloy, shear strength data for various adhesive-adherend combinations 243
 - — , tensile adhesion-strength data for various adhesive-adherend combinations 244

- Amalgams 379
- Amylase, alpha; beta 194
- Amylopectin 185, 186, 195
- Amylose 185, 186
- Anhydrous sodium silicate 296
- Animal glue(s), application 157
 - — as dye leveling agent 175
 - — for woodworking 170
 - — in bookbinding 179
 - — in Calcimine 176
 - — in composition work 177
 - — in finishes 175
 - — in floor polish 181
 - — in matches 180
 - — in paint cleaner 181
 - — in paper 166
 - — in printers' rollers 178
 - — in rayon throwing 175
 - — in sizing rayon yarns 174
 - — in textile processing 173
 - — in the toy industry 180
 - — in wood 169
 - — solutions holding temperature 154
 - — , uses 155
- Antifriction alloys, adhesion to tinned surfaces 450
- Antimony, influence on strength of soldered joints 456
- Application of adhesive 46
- Arabic, gum 198
- Araldite 127, 128, 224, 226, 464
- Asbestos glued by silicate 337
- Ash, adhesion to silicate 285
 - , stresses 118
- Asphaltenes 251
- Asphaltic bitumen 250
 - — as an adhesive 252
 - — , composition 251
 - — , rheology 256
 - — , structure 252
 - — , surface tension 254
- Ball Drop Test 268
- Barrier pH 218, 221
- Beach puncture tester 306
- Beech, adhesion to silicate 286
- Bending tests 476
- Beta amylase 194
- Bingham-Murray viscometer 489
- Bingham solid 36
- Bingham's law 36
- Birch, adhesion to silicate 286
- Birch wood, shear strength data for various adhesive-adherend combinations 243
 - — , tensile adhesion-strength data for various adhesive-adherend combinations 244
- Birefringence 126
- Bitumen(s)
 - , asphaltic 250
 - , — , composition 251
 - , — , structure 251
 - , — , surface tension 254
 - , breaking strength 268
 - , brittleness 274
 - , characterisation 253
 - , contact angle 255
 - , durability 269
 - , elasticity 266
 - , equiviscous temperatures 257
 - , influence of fillers on 270
 - , — — water on 269
 - , — — oxygen on 269
 - , gel-type 259
 - , mechanical properties 274
 - , model systems 266
 - , penetration 260, 262, 264
 - , rheological properties 260, 262, 264
 - , rheology 256
 - , resistance to deformation 267
 - , sol-type 259
 - , viscosity 260, 262
- Bituminous tiles 273
- Boiling point depending on the cohesion of a material 10
- Block shear test 471
- Bloom, gelometer 489
 - , viscometer 489
- Bond strength between metals 452
 - — — —, factors of influence on 452, 453
 - — of rubber, measuring by pull test 394
 - — — silicates 281

- Bond strength testing of corrugated paperboard 306
 Bone glue, uses and sales 156
 Bostik 80
 Brass, adhesion to silicate 284
 Brass plating 408, 417
 Breaking loads for tin-lead solders 458
 Breaking strength of bitumen 268
 Breaking temperature, Fraass' (bitumen) 268
 British gums 184, 187, 188
 Brittleness of adhesives 86
 Brittleness of bitumen 274
 Brookfield viscometer 489
 Brownian motion, two-dimensional 39
 Buna S 421
 — , brittle point; crystallinity 388
 Burst test, Mullen and Cady 306
 Butt joints 92
 — — (strength) 111, 112

 Calcimine, animal glues in 176
 Calcium carbonate and silicate 339
 — lime 354
 Canary dextrines 184, 187, 188
 Cannizzaro's reaction 212, 219
 Capillary rise test for solderability 444
 Carbon black, influence on strength of adhesive bond 395
 Casein, shear strength data for various adhesive-adherend combinations 243
 — , tensile adhesion-strength data for various adhesive-adherend combinations 244
 Cast iron, adhesion to silicate 284
 Catalin 800 132, 138
 Cellulose acetate 239
 Cellulose acetate-butyrate 239
 Cellulose derivatives 196
 — — , water soluble 185, 196
 Cellulose esters 239
 Cellulose-nitrate 239
 — — adhesives 246
 — — , shear strength data for various adhesive-adherend combinations 243
 — — , tensile adhesion strength data for various adhesive-adherend combinations 244

 Cement(s)
 — , (cold setting) properties 370
 — , dental 376
 — , hydraulic 349, 350
 — , inorganic 349
 — , iron 360
 — , Keene's 354
 — , refractory 365
 — , silicate 380, 381
 — , silicate-zinc phosphate 380
 — , sodium silicate 371
 — , Sorel 355, 357
 — , sulfur 361, 362, 363
 — , zinc phosphate 378, 381
 Ceramics, treatment (before soldering) 434
 Chadwick peeling test of soldered joints 481
 — tearing test of soldered joints 460
 Chadwick-type joints in copper, tests on 461
 Chemical replacement tinning 432
 Chilled joint 172, 173
 Chisel test 477
 — — , Koole's 478
 — — of plywood adhesion 483
 Chlorinated rubber 406, 417
 — — , brittle point; crystallinity 389
 Chlorine-containing polymers 413
 Clay-silicate, hot 316
 Cleavage fracture 128
 Cleavage test 476
 — — for metal to metal joints, A.S.T.M. 477
 — — , (woodjoints), french 477
 Close contact test piece 233
 Coal briquettes 273
 Coatings, alloyed 433
 Coatings (tin), electrodeposited 332
 — — , sprayed 333
 Cohesion 10
 — energy 10
 — , molar 26
 Cold flow 234
 Cold-setting adhesives 233
 — cement, properties 370
 Collotype 178

- Colophony flux 431
- Compound, formation during drying (after soldering) 435
- Compound growth in joints (soldering) 449
- Compound layers (soldering), nature of 447
- Concrete, crushing strength 351
- Conditions for adhesion 5
 - for wetting 3
- Contact angle 14
- Conversion of a liquid adhesive into a highly viscous form 52
- Cooling (solder), effect of the rate of — on the adhesion 454
- Cooling time (solder) influence on bond strength between metals 453
- Copper, adhesion to silicate 284
 - , tests on Chadwick-type joints in 461
 - alloys containing beryllium, aluminium, silicon, treatment (before soldering) 434
 - and tin, alloy layer between 448
- Cork, animal glue in composition 177
 - sheets 273
- Corn starch 187
- Corrugated (paper)board 304
 - — boxes, compression strength 318
 - — , crosssections 322
 - — , flexure tests on 321
 - — , manufacture 307
 - — , stiffness factors with 321
- Cotton, adsorption and desorption of water 83
- Covering action by flux (soldering) 429
- Crep strength for soldered joints 458
- Crushing strength of concrete 351
- Cycleweld 224
- Cyclized rubber 80, 406
 - — adhesives 415
 - — , brittle point; crystallinity 389
- Cyclo-rubber 409
- Debye forces 19, 20
- Delamination tests 487
- Dental cements 376
- Dentine 381
- Desmodur R 54, 392, 409, 416, 421
- Desorption, energy 7
- Desorption of water by textiles 83
- Dextrine adhesives 188
- Dextrines 184, 187
 - , canary 184, 187, 188
 - , white 184, 187, 188
- Differential strain 94
- Dilatency 41, 44, 45
- Dispersion forces 18
- Displacement of adherends of lap joints 133
- Dobbie-McInnes viscometer 489
- Double lap joints 107, 108
- Double layer 44
- Douglas fir, stresses 118
- Dried joint 172, 173
- Drying rate of glue films 160
- Durability of bitumen 269
- Durability tests (joints) 485, 486
- Dynamic fatigue 397
- Ebonite 390, 409, 410
 - as a bonding layer 408
 - , used for bonding rubber to metal 411
- Eccentricity of loading 96
- Edge stress 135
- Effect of the edge 106
- Elastic modulus 80
- Elastic-plastic substances 37, 41
- Elasticity of bitumen 266
- Electrochemical action preceding spreading (soldering) 437
- Electrodeposited coatings of tin and solder 432
- Electrostatic forces 19
- Enamel 381
- End-use tests (adhesives) 463
- Energy
 - , free 4
 - , internal 4
 - , potential 38
- Energy density 17
- Energy of adhesion 14
 - of desorption 7
 - of immersion 6
 - of interaction, Keesom 21
 - of interface 4
 - of wetting 4

- Entropy 4
 - of fusion 11
- Enzyme conversion of starch 186, 194
- Epoxy resin 224
- Epoxy-resins 213
- Equiviscous temperature of bitumens 257
- Eutectic solder 457
- Evaporation of solvent from the film 241
- Evaporation, entropy gain on 10
 - , heat needed for 10
- Failing loads, minimum — for joints 234
- Failing loads, minimum mean 227
- Fatigue tests on glued joints 482
- Fernichrome alloy's 122
- Fernico alloy's 122
- Ferranti viscometer 489
- Fiberboard, inner ply solid 328
 - , solid 329
- Fibre-to-rubber bonding 394
- Fiber tubes, cans and drums made with silicates 335
- Fillers, influence on bitumen 270
- Flash point 490
- Flexible adhesive layer 101
- Flooring 273
- Flow characteristics 490
- Flow dependent on temperature gradient (solder) 444
- Flow-resisting properties of ink 58
- Fluid adhesives 397
- Fluosilicates 367
- Flux as a vehicle for reaction products 430
- Flux, electrolytic action 430
- Flux type (solder) influence on bond strength between metals 453
- Fluxes, common 431
- Fraass breaking temperature (bitumen) 268
- Fractionating effect in soldering 445
- Free energy 4
- Friction test (rubber) 396
- Fringe pattern of Catalin model 141
- Frozen stress 126
- Furan derivative resins 212
- Fusion, entropy of 11
 - of surface layers, mutual 57
- Gap-joint models 137, 139
- Gap joints 108, 109
- Gap test piece 233
- Gardner Holdt air bubble-tubes 489
- Gelatine solutions, gelation 51
- Gelation of gelatine solutions 51
- Gelation time 489
- Gel-time of resorcinol-formaldehyde 219
- Gel-type bitumens 259
- Gelva 80
- Glass, adhesion to silicate 284
- Glass, shear strength data for various adhesive-adherend combinations 243
- Glass, tensile adhesion-strength data for various adhesive-adherend combinations 244
- Glass, treatment (before soldering) 434
- Glasses, thermal expansion 121
- Glass surfaces, tensile strength of bonds between 299
- Glass-to-metal adhesion 127
 - seals 121
 - — , development of stress 122, 124
- Glass to steel, adhesive for joining 400
- Glue
 - , animal (application) 157
 - , — (uses) 155
 - , bone (uses and sales) 156
 - , hide (uses and sales) 156
 - , shear and tensile stress 473
- Glue bound papers 169
- Glue films, drying rate 160
 - — (layer), thickness 75, 76
- Glue-glycerin 178
- Glue Manufacturers, National Association of 156
- Glue-sized papers 169
- Glue solutions 151
- Glues, animal 147
 - , vegetable 184
- Gluing, mechanical concept of 148
- Glycerin and litharge mixture 358
- Goland and Reissner, theory 98
- Goldschmidt's compound 206
- G.R.- S adhesive tape, removal 61, 62
 - , brittle point; crystallinity 388
- Gum, adhesion to silicate 285
- Gum arabic 198
 - — , shear strength data for

- various adhesive-adherend combinations 243
 - — , tensile adhesion-strength data for various adhesive-adherend combinations 244
- Gum tragacanth 198
- Gummed cloth 158
 - paper 158
- Gums, British 184, 187, 188
 - , natural 185, 197
- Gutta-percha, brittle point; crystallinity 388
- Hard rubber, shear strength data for various adhesive-adherend combinations 243
 - — , tensile adhesion-strength data for various adhesive-adherend combinations 244
- H.D.I. 392
- Heat of mixing 26
 - — reaction (synthetic resins) 491
 - — wetting 5, 8
- Heat needed for evaporation 10
- Hickory, adhesion to silicate 286
- Hide glue 151
 - — , jelly strength 153
 - — , uses and sales 156
- Holding temperature for animal glue solutions 154
- Hooke's law 38
- Hot-setting adhesives 227
- Hycar, brittle point; crystallinity 388
- Hydraulic cements 349, 350
- Hydrocal 353
- Immersion, energy of 6
- Impact tests on glued joints 482
- Induction forces 19
- Inorganic adhesives 278
 - cements 349
- Interaction, Keesom energy 21
- Interface, energy of 4
- Internal energy 4
- Internal stresses in the adhesive 84
- Iron cements 360
- Isochromatics 137, 138
- Isoclinics 140
- Isocyanates 391, 408, 416
- Isocyanate solution 420
- Isotropic point 135, 138
- Jelly strength 147, 489
 - — of hide glue 153
- Joint factor 98, 471
- Joint strength 77
 - — , german test 476
 - — , shearing 76
 - — , tests 465
- Joint(s)
 - , butt 92
 - , — (strength) 111, 112
 - , chilled 172, 173
 - , double lap 107, 108
 - , dried 172, 173
 - , gap 108, 109
 - — , German scarf 474
 - , lap 93 ff.
 - , "Redux" 92
 - , minimum failing loads 234
 - , scarfed 95, 472
 - , simple overlap 224
 - (soldered), compound growing in 449
 - — , structure of the bond 446
 - , starved 171, 172
 - , stresses (experimentally) 129
 - , — in 91
 - , time-factor effect on strength 114
 - , torsion 92
- Joining capacity of soldering systems 440
- Kaolin clay suspensions, gel strength 312
 - — — , plasticity 312
- Keene's cement 354
- Keesom energy of interaction 21
 - forces 19, 20
- Knife test for plywood 484
- Kollagrams 441
- Kollagraph 440
- Koresin 57, 393
- Kovar 123
- Labeling 333
- Laminated paper 273
- Laminated wood, stresses 116
- Lap joints 93 ff.

- Lap joints, close contact 468
 - —, displacement of the adherends 133
 - —, double lap 107, 108
 - —, loaded 95
 - — under compressive loads 471
 - — under tensile load 468
 - —, unloaded 95
 - — with gap 468
 - —, Volkersen's analysis 97
- Latex-albumen-sulphur mixes 412
- Latex-based adhesives 398, 399
- Latex-blood albumen 408
- Latex-resorcinol 421
- Latex-resorcinol-formaldehyde 420
- Latex-sulphur-blood-albumen 409
- Latex, vulcanizing 398
- Lead, adhesion to silicate 284
- Life tests on lap joints (soldered) in tinplate 459
- Lime mortars 354
 - , reaction with sodium silicate 375
- Liquid adhesive, conversion into a highly viscous form 52
- Liquids, tensile strength 113
- Litharge 358
- Loading tests (stepped) on lap joints in tinplate 459, 460
- London forces 18, 23
- Long range molecular forces 115

- Macromolecules of opposite polarity 32
- Magnesium lime 354
- Mahogany, stresses 118
- Maker-coat 161
- Maltenes 251
- Maple 150
 - , adhesion to silicate 284
- Maxwell relaxation law 131
- Mechanical adhesion 47
- Mechanical concept of gluing 148
- Mechanical properties of bitumen 274
- Melamine-formaldehyde adhesives 208
 - resins 221
- Melocol H, glue 115
- Metal to metal bonding by adhesives 223
- Metal to wood bonding by adhesives 226
- Metalbond 224

- Metal-metal joints, shear strength 225
- Metal-rubber test piece 394
- Metals, bond strength between 452
 - , solderability 442
 - , thermal expansion 121
 - , wetting of — by tin and solder 434
- Methacrylic esters 239
 - resins 238
- Mica glued by silicate 338
- Mild steel, adhesion to silicate 284
- Mineral wool glued by silicate 338
- Miscibility depending on the cohesion of a material 10
- Mixing, heats of 26
- Model systems of bitumens 266
- Molar cohesion 26
- Molecular forces 9, 18
 - —, long range 115
- Molecule, size 21
- Mortars, lime 354
- Mullen and Cady burst test 306
- Mullen test 316

- National Association of Glue Manufacturers 156
- Natural gums 185, 197
- Natural rubber 421
 - — adhesive tape, removal 61, 62
 - —, brittle point; crystallinity 388
- Neoprene 417
 - , brittlepoint; crystallinity 388
 - , shear strength data for various adhesive-adherend combinations 243
 - , tensile adhesion-strength data for various adhesive-adherend combinations 244
 - , vulcanizing solutions 405
- Neoprene-type rubbers 404
- Newtonian liquids 60
- Newton's law 34, 36
- Nickel, adhesion to silicate 284
- Nitrile rubber 406
 - —, brittle point; crystallinity 388
- Non destructive tests of glued joints 484
- Nonex glass 123
- Non-Newtonian liquids 60
- Non-polar molecule 23

- Oak, stresses 118
- Organic adhesives 147
- Overlap joint, simple 224
- Oxide, removal of—by flux (soldering) 429
- Oxygen, influence on bitumen 269

- Paint film, shear test 470
- Paper
 - box-flaps, sealing 330
 - coatings 168
 - glued by silicate 337
 - joints 150
 - , laminated 273
 - manufacture 166
 - , picking (plucking) of 65
 - sizings 167
 - , wetting by sodium silicate 290
- Paperboard
 - boxes, compression strength 318
 - , corrugated 304
 - — , cross sections 322
 - — , flexure tests on 321
 - — , production 305
 - — , stiffness factors with 321
 - — , testing bond strength 306
 - , specifications and tests 305
 - , structural tests 318
- Paper-phenolic laminate, shear strength
 - data for various adhesive-adherend combinations 243
 - — , tensile adhesion-strength data for various adhesive-adherend combinations 244
- Parquet floors 273
- Patents referring to rubbery adhesives 425
- Peeling tests 478
 - — , A.R.L. 479
 - — of soldered joints, Chadwick 481
 - (tackiness) 70
- Penetration (bitumens) 260, 262, 264
- Penetrative powers of solders 445
- Perbunan, brittle point; crystallinity 388
- Persimmon, adhesion to silicate 286
- Phenol-formaldehyde resin 132, 134, 215
 - — bonded plywood 228
- Phenolic glue, setting time for a (typical) 217, 218
- Phenolic resin adhesives 203

- Photoelastic investigation of Catalin 800 138
 - — — the stress 127
- Photoelastic tests 134
- Photogelatin 178
- pH required to cause setting 218
- Physical testing of adhesion and adhesives 463
- Picking (plucking) of paper 65
- Piercing test (plywood) 484
- Plaster of Paris 352, 353
- Plastic cement, properties 370
- Plastic flow of an adhesive 79
- Plasticizer for dextrines 191
- Plasticizing of dextrine adhesives 189
- Pliobond 105, 224
- Plywood 273
 - adhesion, chisel test of 483
 - adhesive test joints 468
 - glue, urea-formaldehyde resin 228
 - , glued with a urea-formaldehyde resin glue, fortified with melamine resin, shear tests 230
 - — — — — , fortified with resorcinol, shear tests 229
 - joints 75
 - , knife test for 484
 - , phenol-formaldehyde resin bonded 228
 - , piercing test 484
 - test piece 227
- Poiseuille's law 34
- Poisson's ratio 103, 130
- Polarity 22
 - , active positive 23
 - , active negative 23
- Polishing wheels 163
- Polybutadiene, brittle point; crystallinity 388
- Polyethylene, brittle point; crystallinity 388
- Polyisocyanates 406
- Polymerisation in situ 246
- Polymers, adhesion to cellulose 31
- Polystal 212

Rubber

- hydrochloride 406
- — , brittle point; crystallinity 389
- in bitumen 271
- latex and silicate 342
- , natural 421
- (natural), brittle point, crystallinity 388
- , nitrile 388, 406
- , shear strength data for various adhesive-adherend combinations 243
- solutions 398
- , tackiness-tester 70
- , tensile adhesion-strength data for various adhesive-adherend combinations 244
- to brass bond 418
- to fibres 419
- to metals, adhesion 407
- to metals, bond 409
- to metals, ebonites used for bonding 411

Rubbery adhesives 386
 — — , patents referring to 425

Rudeloff's tensile test for wood joints 466

Sago starch 187

Salt conversion of starch 193

Scarfed joint 95, 472

Scarf joint, German 474

Schwingmetall 416

Sealer, automatic 331

Sealing alloy's, thermal expansion 121

Sealing of paper box-flaps 330

Segregation of tin-copper compound at the bond 450

Setting characteristics of silicates 293

- of the adhesive 71
- of thermoplastic resin adhesives 240
- , pH required to cause 218
- time for a phenolic glue 218
- — for a typical phenolic glue 217

Shear

- by bending (beam) 474
- distribution of a laminate 120
- — , longitudinal 140

Shear in glue 473

- modulus 99, 103
- , production by twisting 475
- strength data for various adhesive-adherend combinations 243
- — of metal-metal joints 225
- — of resin glue 75
- stress concentration, factor 101, 130
- — plotted against joint factor, apparent 470
- with overlap, variation of apparent 470
- tests (joints) 467
- , tests in pure 475
- — , distribution of 464
- — of paint film 470
- — on plywood, glued with a urea-formaldehyde resin glue, fortified with melamine resin 230
- — on plywood, glued with a urea-formaldehyde resin glue fortified with resorcinol 229

Silicate

- adhesives 309
- — used on paper 304
- bonds 325
- cements 380, 381
- — , porosity 366

Silicates

- , bond strength 281
- , resistance to pests 296
- , setting characteristics 293
- , tack 287
- , tensile strength 281
- , viscosity 286, 294
- , wetting properties 290
- , working properties 286

Silicate-zinc phosphate cements 380

Silicone resins 213

Silicones 6

Silicious gels 366

Size of the molecule 21

Sizing materials (gelatin, glue) applied to paper 167

Slag concrete, crushing strength 351, 352

Sodium silicate 278

- Sodium silicate adhesive, clay content 315
 - — — , constitution 280
 - — — , properties 280
 - — — , temperature 315
 - — — , viscosity 315
- Sodiumsilicate
 - — , application to glass 299
 - — , — to metals 300
 - — , — to wood 302
- Sodium silicate bonds, strength 284
 - — cement 371
- Sodium silicate-clay adhesives, control
 - — — — of hot 309
 - — — — , mixing 311
 - — — — , viscosity 313
- Sodium silicate, industrial use 305
 - — , reaction of lime with 375
 - — , reaction with paper 298
 - — , solution, surface tension 291
 - — , solution, tackiness (of oil and) 288, 289
 - — , surface tension 291
 - — , viscosity 286, 287, 288, 289
 - — , wetting coefficient 291
- Solder
 - , composition, effect on the shear strength of soldered joints 456
 - , ease of displacement 430
 - , eutectic 457
 - , height of climb upon a metal 444
 - , measurement of wetting by 440
 - , spreading tests (apparatus; results) 439
- Solderability of metals 442
 - , area of spread tests 438
 - , capillary rise test 444
- Soldered joints, adhesion in 427
 - — , Chadwick peeling test 481
 - — , Chadwick tearing test 460, 461
 - — , cohesion and adhesion 428
 - — , creep strength 458
 - — , influence of surface condition 428
 - — in tinfoil, strength 456
 - — , strength 455
 - — , structure of the bond 446
- Soldered lap joints, tensile test 458
- Soldering, action of flux 429
 - , fractionating effect in 445
 - systems, jointing capacity 440
- Solders in bar form, strength 455
 - , penetrative powers 445
 - , Schumacher's apparatus for testing 444
 - , strength 455
 - , surface tension 439
- Solidification of thermosetting resins 210
- Solids content 494
- Sol-type bitumens 259
- Solubility depending on the cohesion of a material 10
- Solvent, evaporation from the film 241
- Solvents in adhesive layers, rheological aspects 53
- Sorel cement, 355, 357
- Specific adhesion 47
- Sprayed tin coatings 433
- Spreading and alloying (solder) 438
- Spreading of solder 436, 437, 438
- Spreading qualities of solders, apparatus for determining 439
- Spreading tests (solder) results 439
- Spread tests for solderability, area of 438
- Spruce, stresses 118
- Stability of adhesives 490
- Stainless steel, adhesive to 243
 - — , shear strength data for various adhesive-adherend combinations 243
 - — , tensile adhesion-strength data for various adhesive-adherend combinations 244
- Stannising 433
- Starch and silicate 340
 - derivatives 196
 - — , water soluble 184, 196
 - oxidations 198
- Starch(es) 185
 - , acid hydrolyzed 184, 198
 - , alkali conversions 192
 - , degradation of 197
 - , enzyme conversion 186, 194

- Starch(es), enzyme degraded 184
 — , gelled 184
 — , oxidized 184, 198
 — , salt conversion 193
- Starved joint 171, 172
- Static problems 91
- Steel (mild), adhesion to silicate 284
- Steel (stainless), shear strength data for various adhesive-adherend combinations 243
 — — , tensile adhesion-strength data for various adhesive-adherend combinations 244
- Stefan's formula 112
- Strength of a rubber adhesive bond 393
 — , of solders and soldered joints 455
- Stress concentration 93, 111
 — — factor 97, 132, 142
 — — —, (shear-and tearing-) 130
- Stress distribution in composite joints 141
- Stress-optical coefficient 137
- Stress-trajectories 127, 140
- Stress(es)
 — , development during cooling (glass-to-metal seal) 122
 — , edge 135
 — , frozen 126
 — in joints 91
 — in joints, (experimentally) 129
 — in laminated wood 116
 — in the adhesives, internal 84
 — in two-layer beams of timbers 118
 — , photoelastic investigation 127
 — , residual 115
 — , variation of radial, tangential and longitudinal — of glass cylinder and metal rod 125
- Stripping tests 478
- Structure of the bond in soldered joints 446
- Sulfur cements 361, 362, 363
 — — , properties 363
- Surface capillarity and spreading (soldering) 437
- Surface-coated abrasives 161
- Surface roughness, effect on spreading (soldering) 436
- Surface sizing 167
- Surface tension 53, 54
 — — tension effects by flux 431
 — — of sodium silicate solution 291
 — — of solders 439
 — — of sodium silicate 291
- Surface treatment of roads 273
- Surgery plasters 60
- Synthetic resin adhesives 201
 — — —, (production and sales) 202
- Synthetic resins 163
- Tack of printing ink 58
 — — — , measure 69
 — of silicates 287
- Tackifiers 392
- Tackiness 55, 56, 64, 65
 — , measurement 67
 — of oil and sodium silicate solutions 288
- Tackiness-tester for rubber 70
- Tackmeter 68
- Tacky adhesives, tests 485
- Tapioca starch 187
- Tearing stress concentration 103
 — — — factor 130
- Tearing test of soldered joints, Chadwick 460, 461
- Temperature, influence on bond strength between metals 452
 — — — the properties of adhesives 85
- Tensile strength 10, 11
 — — data for various adhesive-adherend combinations 244
 — — of bonds between glass surfaces 299
 — of glue line (sodium silicate) 292
 — — of liquids 113
 — — of silicates 282
 — — tester 283
 — — , variation with thickness of adhesive 466
- Tensile stress 473
 — — distribution 117
 — — — of a laminate 120
- Tensile test for lap joints (soldered) 458

- Tension tests (joints) 465
- Test piece, close contact; gap 233
- Tests for solderability, area of spread 438
- Theory of Goland and Reissner 98
 - -- similarity of structures 130
- Thermal contraction, differential -- of adherends and adhesive 116
 - -- , unit 120
- Thermal expansion of glasses, metals sealing alloys 121
- Thermoplastic adhesives 201, 234, 412
 - -- , application 245
- Thermoplastic resin adhesives, setting 240
- Thermosetting adhesives 201
 - resins, solidification 214
- Thickness, influence on bond
 - of adhesive layer influence on strength of adhesive bond 414
 - (of coating) influence on bond strength between metals 453
 - of glue film (layer) 75, 76
 - of the layer, influence 7
- Thin adhesive layers 76, 78, 99
- Thin inflexible adhesive layers 106
- Thin joints, strength 78
- Thixotropic adhesive 50
 - systems 42
- Thixotropy 41, 43
- Threshold pH 218
- Tiles, bituminous 273
- Time-factor, effect on the strength of joints 114
- Tin, adhesion to silicate 284
 - and copper, alloy layer between 448
 - coatings "pores" in 435
- Tin-copper compounds 447
 - -- , segregation at the bond 450
 - -- , solubility in tin 448
- Tin-iron compounds 447
- Tin-lead alloys 457
 - solders, breaking loads for 458
- Tinned surfaces, solderability 431
- Tinning medium (solder) influence on bond strength between metals 453
- Tinplate, life tests on lap joints in 459
 - , stepped loading tests on lap joints in 459, 460
- Topography of absorbing layers 7
- Top-sizer 162
- Torsion joints 92
- Tragacanth, gum 198
- Trolon 134
- Tub sizing 167, 168
- Typly 414
- Ty-ply Q 409
- Unit thermal contraction 120
- Urea-formaldehyde adhesives 206
- Urea-formaldehyde resins 220, 228
 - -- , fortified by melamine resin 232
 - -- , pot-lif of a 214
 - -- glue, fortified with melamine resin, shear tests on plywood 230
 - -- -- -- -- resorcinol, shear tests on plywood 229
 - -- plywood glue 228
- Usable Life 489
- Vegetable adhesives 184
 - glues 184
- Vinnapas 80
- Viscometers 286, 488, 489
- Viscose rayon, adsorption and desorption of water 83
- Viscosities of woodworking glues 171
- Viscosity (animal glues) 488
 - (bitumens) 260, 262
- Viscosity of silicates 286, 294
- Voigt element 261
- Volatility 10
- Vulcabond 80
- Vulcabond R 415
- Vulcabond T X 417
- Vulcanizing latex 398
 - -- mixtures 401
 - solutions of Neoprene 405
- Wallboard 334
- Walnut, adhesion to silicate 284
 - , stresses 118
- Walthers formula 256
- Wash board 323
- Water, adsorption and desorption by textiles 83

- , influence on bitumen 269
- Wetting by solder, measurement 440
 - coefficient, sodium silicate 291
 - , conditions 3
 - , energy of 4
 - , heat of 5, 8
 - of metals by tin and solder 434
 - of paper by sodium silicate 290
 - properties of silicates 290
- White dextrans 184, 187, 188
- Wood, adhesion to silicate 284
- Wood joints 48
 - — , Rudeloff's tensile test for 466
- Wood, stresses in laminated 116
- Wood to wood bonding by adhesives 226
- Woodworking glues, viscosity 171
- Woodworking, animal glue for 170
- Wool (mineral, glued by silicate 338
- Working properties of silicates 286
- Xylonite 135
- Yield value 43
- Young's modulus 99, 103, 117, 118, 120
130, 140
- Zinc chloride flux 431
- Zinc phosphate cements 378, 381



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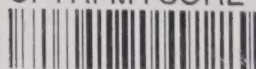
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